ISSN 1063-7826, Semiconductors, 2020, Vol. 54, No. 14, pp. 1840–1842. © Pleiades Publishing, Ltd., 2020.

NANOSTRUCTURE TECHNOLOGY

Structure and Magnetic Properties of the FeCo–C Films Reduced by Carbohydrates

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Received June 19, 2020; revised June 19, 2020; accepted July 17, 2020

Abstract—The structural and magnetic properties of FeCo–C films produced by electroless plating with different carbohydrates as reducing agents have been investigated. The surface morphology and coercivities of FeCo–C films are dependent on the iron content and type of reducing agent. The local magnetic anisotropy field value increases with a decrease in Fe content. For all systems, deposits with good soft magnetic properties were obtained, with coercivities less than 12 Oe and saturation magnetizations close to 240 emu/g for FeCo–C film with 30% cobalt. The best soft magnetic properties corresponded to the deposits with bcc structure and grain sizes less than 20 nm.

Keywords: FeCo–C alloy, electroless deposition, magnetic properties

DOI: 10.1134/S1063782620140079

1. INTRODUCTION

Soft magnetic films have been widely used in the fields of magnetic recordings, magnetic sensors [1, 2]. As a kind of typical soft magnetic materials, CoFe alloy films exhibit superior magnetic properties such as high Curie temperature, low coercivity, low magneto-crystalline anisotropy, high permeability and high saturation magnetization (can reach up to 245 emu/g). The magnetic properties of CoFe films depend on their morphology, crystal structure and composition. Although there are many methods available for the preparation of CoFe films, such as sputtering, molecular beam epitaxy, ion beam deposition, electrodeposition and so on [3–5]. Electroless plating shows low cost and no size or shape limit for the preparation of nano-scale films. On one hand, electroless deposition represents a simple, cost-effective way of fabricating FeCo film [6]. However, use of conventional reducing agents (sodium hypophosphite or borohydride, hydrazine) leads to significant contaminations with phosphorus and boron in deposited films damaging the magnetic performance. On the other hand, researchers found that polysaccharides (e.g., chitosan, cellulose) could be an efficient, low-cost, and environmental alternative to conventional reducing agents [7]. Herein, we report a facile and highly efficient method for fabricating nanostructured FeCo films. The FeCo alloy was directly synthesized on copper supports via electroless deposition with different carbohydrates as reducing agents (arabinogalactan, starch, sucrose), the composition of which can be easily controlled by changing the concentration of metal salt in the solution. Magnetic studies of these films which exhibit high saturation magnetization are also reported in this work.

2. EXPERIMENTAL

The FeCo–C films were prepared by electroless reduction of metals from aqueous solutions of the corresponding salts at 80°C. Each plating bath was comprised of source metal ion (cobalt(II) sulfate and ammonium iron(II) sulfate), metal chelator (sodium citrate), and reducing agent. The pH value was adjusted by adding NH_4OH solution. We used several

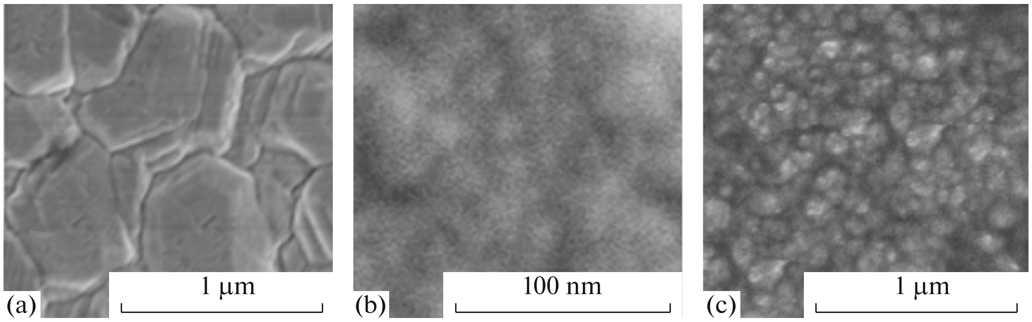

Fig. 1. SEM imagines of the FeCo films, produced with sucrose (a, b) and arabinogalactan (c) as reducing agents (a) Fe/(Co+Fe) ~ 0.14; (b) Fe/(Co+Fe) ~ 0.94 and (c) Fe/(Co+Fe) ~ 0.92.

types of reducing agents: arabinogalactan—natural polysaccharide, corn starch and sucrose.

The morphology of the deposited films was analyzed with scanning electron microscopy (SEM: Hitachi S-5500). Compositional analyses were performed via energy dispersive X-ray spectroscopy (EDS) associated with SEM. Structural analysis of the studied systems was carried out using X-ray diffraction (Cu K_α). The magnetic properties were investigated using a vibrating sample magnetometer. Information on local anisotropy field H_a is obtained from investigation of approach magnetization to saturation law.

3. RESULTS AND DISCUSSION

The surface morphologies of the obtained samples are shown in Fig. 1. The morphology of the samples can be varied by changing the Fe/Co molar ratio. With increase of Fe content in the film for all types of reducing agents, the surface morphology of the samples changed greatly, as shown in Figs. 1a and 1b. The metallized surfaces consist of agglomerates of spheroidal particles for FeCo–C films with Fe/Co < 0.4. Replacing the arabinogalactan with a sucrose produced surfaces comprised of larger, more faceted metal particles in case Fe/Co > 0.5. It is found that with using arabinogalactan as reducing agent, the surfaces of the electroless deposited films are generally smooth and uniform.

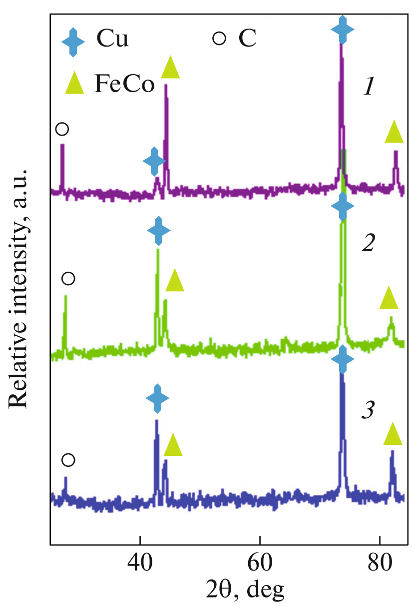

Fig. 2. XRD patterns of the FeCo–C films (Co content 40 at %) produced with different reducing agent: starch (*1*), arabinogalactan (*2*), sucrose (*3*).

The element mapping analysis of Fe, Co, and C also measured by the EDS technique reveals that Fe, Co, and C are evenly distributed throughout the film. The glycosidic bonds forming the carbohydrates molecules are stable at a low temperature. However, synthesis of FeCo–C films carried out at bath temperature 80°C at in an alkaline medium. The carbohydrates degradation occurs at the ends of the molecules under such conditions. Aldehyde groups at the ends of molecules have reduction properties. Thus, the monosaccharide unit is separated and then oxidized to a carboxylic acid. Therefore, it can be assumed that the formation of a metal film is due to decomposition of the carbohydrates. The XRD patterns of FeCo–C films revealed peaks that perfectly matched with those of the bcc phase of CoFe or fcc-Cu substrate and no oxides phases were observed within the detection limits of the X-ray diffractometer. Peak located at 27.5° can be assigned to carbon. There was no obvious difference among the XRD patterns of films prepared with different reducing agents (Fig. 2). The average crystallite size calculated using the Scherrer formula for the all types of reducing agents was in rage 10–27 nm. The bcc structure is found to be stable even for films with very high concentration of Co (~0.85) beyond the thermodynamically stable bcc regime for bulk $Fe_{1-x}Co_x$ alloys ($0 < x < 0.25$ [8]).

Magnetic parameters such as the saturation magnetization, the coercivity of the films were studied as a function of Fe content. The data show a strong dependence of the magnetic parameters on the iron content.

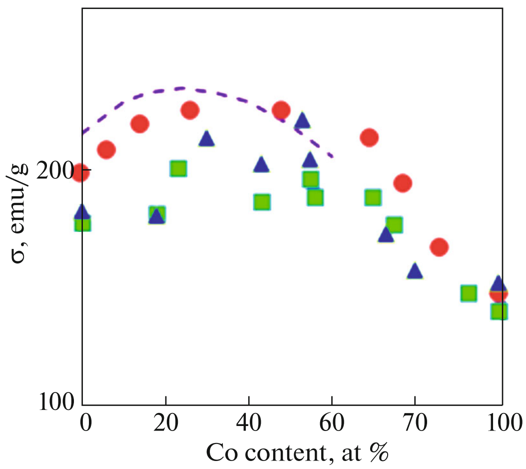

Fig. 3. The saturation magnetization of FeCo films produced with different types of reducing agent as a function of cobalt content (circles—sucrose as reducing agent; triangles—corn starch; squares—arabinogalactan). Data [2] was shown by dashed line.

The saturation magnetization dependences of the FeCo–C films as expected were nonlinear (Fig. 3). The produced FeCo–C films demonstrated significantly better saturation magnetization values (**σ**) and less contaminations, compared to those for the sample preparing with conventional reducing agent (sodium hypophosphite).

The **σ** value for films reducing with hypophosphite does not exceed 190 emu/g due to phosphorus contaminations. In cases FeCo–C films reduced with carbohydrates the σ values are 205, 235 and 240 emu/g for arabinogalactan, starch and sucrose respectively. The magnetization values of the samples are relatively higher than those of the usual FeCo–C alloy. It is mainly due to carbon is not included in the FeCo lattice. For all systems, deposits with good soft magnetic properties were obtained, with coercivities less than 12 Oe and saturation magnetizations close to 240 emu/g for the $Fe_{70}Co_{30}$ film. The best soft magnetic properties corresponded to the deposits with bcc structure and grain sizes less than 20 nm.

Approach magnetization to saturation in the log-log plot follows $M(H) \sim (H)^{-2}$ dependence for H from 3 to 12 kOe for all film series. Magnetization approaches to saturation as $M \sim H^{-a}$ with $0.75 < a < 1.1$ in the field range from 1 to 3 kOe. Such behavior indicates that the FeCo alloy is nanocrystalline [9]. It was found that the local anisotropy field for all series of FeCo alloys depends on Fe content. The H_a value increases with a decrease in Fe content. The Ha value increases with a decrease in Fe content and was in range 360–2000 Oe. Further optimization of fabrication condition is in progress aimed at further improving soft magnetic and dynamic properties.

4. CONCLUSIONS

In summary, a simple, eco-friendly and efficient route for obtaining high-induction FeCo–C films has been explored. The FeCo–C films were synthesized by electroless plating with arabinogalactan, starch and sucrose as nontoxic reducing agents. It was found that Fe concentration and type of reducing agent affect the surface morphology. Maximum of saturation magnetization magnitude is 240 emu/g for FeCo–C film with 30% cobalt. The local anisotropy field value increases with a decrease in Fe content for all series of FeCo–C alloys.

ACKNOWLEDGMENTS

Measurements by electron microscopy were performed on equipment of the Krasnoyarsk Regional Center of Research Equipment of Federal Research Center "Krasnoyarsk Science Center SB RAS".

FUNDING

This work was supported by the Russian Foundation for Basic Research, the Government of the Krasnoyarsk Territory, the Krasnoyarsk Regional Fund for the Support of Scientific and Technical Activities (project no. 18-42-240006 Nanomaterials with magnetic properties determined by the topological features of the nanostructure).

CONFLICT OF INTEREST

The authors have no conflicts of interest to declare that are relevant to the content of this article.

REFERENCES

1. M. Alper, H. Kockar, T. Sahin, and O. Karaagac, IEEE Trans. Magn. **46**, 390 (2010).
2. C. Rizal, J. Kolthammer, R. K. Pokharel, and B. C. Choi, J. Appl. Phys. **113**, 113905 (2013).
3. P. Wetzel, P. Bertoncini, D. Berling, A. Mehdaoui, B. Loegel, D. Bolmont, G. Gewinner, C. Ulhaq-Bouillet, and V. Pierron-Bohnes, Surf. Sci. **499**, 210 (2002).
4. S. Amsarajan and B. R. Jagirdar, J. Alloys Compd. **816**, 152632 (2020).
5. T. Yanai, K. Shiraishi, Y. Watanabe, T. Ohgai, M. Nakano, K. Suzuki, and H. Fukunaga, J. Appl. Phys. **117**, 17A925 (2015).
6. K. Sun, K. Wang, T. Yu, X. Liu, G. Wang, L. Jiang, Y. Bu, G. Xie, Int. J. Hydrogen Energy **44**, 1328 (2019).
7. S. Machado, S. L. Pinto, J. P. Grosso, H. P. A. Nouws, J. T. Albergaria, and C. Delerue-Matos, Sci. Total Environ. **445–446**, 1 (2013).
8. *Magnetic Properties of Metals d-Elements, Alloys and Compounds, Data in Science and Technology,* Ed. by H. P. J. Wijn (Springer, Berlin, Heidelberg, 1991)
9. R. S. Iskhakov and S. V. Komogortsev, Bull. Russ. Acad. Sci.: Phys. **71**, 1620 (2007).