UDC 669.018.5:620.187

S. I. Ryabtsev*, P. S. Gusevik, K. E. Kurdyukova

Oles Honchar Dnipropetrovsk National University, Dnipropetrovsk, Ukraine
**e-mail: siryabts@mail.ru*

STRUCTURE AND PHYSICAL PROPERTIES OF Fe-Bi-Pt FILMS IN METASTABLE STATE

The regularities of formation of FeBiPt metastable film structures obtained by modified three-electrode ion-plasmas sputtering method (IPS) were researched in this work. X-ray analysis showed that in the as-deposited films there is formed a mixture nanocrystalline phase (the size of coherent scattering region L = 2-4 nm) and traces of BiPt and rhombohedral Bi. The film heat treatment in a vacuum at a temperature above 750 K leads to its oxidation. Heat treatment leads to formation α-Fe supersaturated solid solution rhombohedral Bi phase and traces of BiPt phase. The temperature dependence of the resistivity analysis revealed that the Fe-Bi-Pt activation energy of the phase transitions is EA ~ 7000-13000 K for subject to composition. After heating the Fe-16 ат.%Bi-20 ат.%Pt films to the temperatures above 730 K and subsequently cooled to a temperature of 430 K is an abrupt change in resistance. Analysis of the demagnetization curves showed that the hysteresis of the magnetization is observed only in the Fe (9 at. %) – Bi (6 at. %) - Pt films.

Keywords: FePt films, ion-plasma sputtering, hard magnetic materials, metastable state.

У роботі досліджені закономірності формування метастабільних структур плівок Fe-Bi-Pt отриманих модернізованим методом трьохелектродного іонно-плазмового розпилювання (ІПР). В результаті рентгеноструктурного аналізу встановлено, що у тільки-но напилених плівках Fe-(9-16 ат.%)Bi-(6-20 ат.%)Pt утворюється суміш нанокристалічної фази (розмір області когерентного розсіювання L = 2-4 нм) слідів нерівноважного кубічного Bi. Термообробка в вакуумі при температурі понад 750 К призводить до окислення плівки та утворення пересиченого твердого розчину FePt і виділень фаз ромбоедричного Bi і слідів фази BiPt з кубічною решіткою. Аналіз кривих температурної залежності електроопору плівок дозволив встановити, що для плівок Fe-Bi-Pt енергія активації фазових переходів складає ЕА~7000-13000 К в залежності від складу. При нагріві плівок Fe-16 ат.%Bi-20 ат.%Pt до температури більше 730 К та подальшому охолодженні до температури 430 К відбувається стрибкоподібна зміна електроопору. Аналіз кривих розмагнічування плівок показав, що гістерезис намагнічування спостерігається тільки в плівках Fe (9 ат. %) - Bi (6 ат. %) - Pt.

Ключові слова: плівки FeBiPt, іонно-плазмове розпилювання, магнітотверді матеріалі, метастабільній стан.

В работе исследованы закономерности формирования метастабильных структур пленок Fe-Bi-Pt полученных модернизованным методом трехэлектродного ионно-плазменного распыления (ИПР). В результате рентгеноструктурного анализа установлено, что в свеженапыленных пленках Fe-(9-16 ат.%)Bi-(6-20 ат.%)Pt образуется смесь нанокристаллической фазы (размер области когерентного рассеяния L=2-4 нм) и следов неравновесного кубического Bi. Термообработка в вакууме при температуре выше 750 К приводит к окислению пленки и образованию пересыщенного твердого раствора FePt и выделений фаз ромбоэдрического Bi и следов фазы BiPt с кубической решеткой. Анализ кривых температурной зависимости электросопротивления пленок позволил установить, что для пленок Fe-Bi-Pt энергия активации фазовых переходов составляет ЕА~7000-13000 К в зависимости от состава. При нагреве пленок Fe-16 ат.%Bi-20 ат.%Pt до температуры свыше 730 К и последующем охлаждении до температуры 430 К происходит скачкообразное изменение сопротивления. Анализ кривых размагничивания пленок показал, что гистерезис намагничивания наблюдается только в пленках Fe (9 ат. %) - Bi (6 ат. %) - Pt.

Ключевые слова: пленки FeBiPt, ионно-плазменное распыление, магнитотвердые материалы, метастабильное состояние.

1. Introduction

Significant interest in investigating FePt and FeBi alloys is due to the manifestation of a high coercivity and residual magnetization which is typical for high magnetic materials [1-3]. The manifestation of a high coercivity enables to use this material as magnetic elements for microelectronic devices and a high-density information recording systems [4]. Recently research is conducted for improving the magnetic properties of known magnetic materials by heat treatment and obtaining conditions influencing on the domain structure. It has also become topical the study of magnetic samples obtained under non-equilibrium conditions in the film form. Such films are amorphous or nanocrystalline compounds in which the important role played by the size effects. These effects have a direct impact on the samples physical properties. This paper investigates the structure, phase composition and physical properties of the Fe-Bi-Pt films, as well as the influence of the deposition conditions and heat treatment on the original structure and properties.

2. Materials and Methods

Studies was carried out on thin films, with compositions (at.%): $Fe_{64}Pt_{20}Bi_{16}$ (composition 1); $Fe_{71}Pt_{20}Bi_9$ (2); $Fe_{80}Pt_{11}Bi_9$ (3); $Fe_{71}Pt_{20}Bi_9$ (4-5). Films with thicknesses about d ~ 150 - 65 nm was obtained by a modernized three-electrode ion-plasma sputtering [5] under various deposition conditions. The effective cooling rate for this method is theoretically estimated as 10^{12} - 10^{14} K/s [6] and associated with the relaxation of individual atoms on the substrate. Inert Ar was used as the orifice gas. The film thickness was determined by the gravimetric method by weighing the substrate before and after spraying.

The deposition of the films was carried out on NaCl single crystals and pyroceramics (sitall) substrates. The films deposited on NaCl substrates were used for studies of phase composition in the initial and heat-treated states. The phase composition was carried out by X-ray analysis using the Debye camera with filtered Co-radiation and transmission electron microscopy (on the samples received under reduced thickness and deposition time). The lattice periods were estimated with an accuracy of ± 0.001 nm.

The physical properties and thermal stability were examined for the films deposited at pyroceramics substrates. The films surface resistivity was measured by four-probe method with continuous heating in a vacuum about ~ 10 mPa with controlled heating rates between 4 and 20 K/min. The activation energy calculation of phase transitions was conducted by Kissinger method [7], by analyzing the phase transition temperature displacement with heating rate changing. The films coercive force H_c was investigated by vibration magnetometer in the maximum magnetizing field about 0.5 T, with parallel and perpendicular orientation to the film surface.

3. Results and discussion

X-ray analysis results of the initial and heat treated films are shown in Table. 1. The nanocrystalline phase FePt (with CSR size L ~4-2.8 nm) trace of cubic Bi and trace of Bi_2Pt were observed in the initial FePtBi films (composition 1-2). After heat treatment in vacuum at a temperature of 770-780 K we see fcc FePt (a=0.3769-0.377 nm), traces of rhomb Bi, traces of Bi_2Pt and there is a grain growth of the nanocrystalline phase (CSR size increases to 45-30 nm). In the FePtBi films (composition 3-4) as shown X-ray studies, in the initial state there are a mixture of the nanocrystalline phase (with CSR size L ~2.1-2.2 nm) and traces of FeO and Bi_2Pt. After heat treatment in vacuum at a

temperature of 770-780 K we saw fcc FePt (a = 0.3724 - 0.3707 nm), and equilibrium rhombohedral Bi phase and traces of FeO (Fig. 1a, b).

Table 1

Freshly deposited and heat-treated films phase composition

Composition (at.%)	d, (nm)	Films phase composition		
		The annealing temperature	In initial state	After heat treatment
$Fe_{64}Pt_{20}Bi_{16}$ (1)	130	780 K	NCP of FePt (L=4.0 nm)+ trace of cubic Bi + trace of Bi_2Pt	supersaturated solid solution of FePt (a=0.3769 nm) + trace of rhomb Bi + trace of Bi_2Pt
$Fe_{71}Pt_{20}Bi_9$ (2)	150	770 K	NCP of FePt (L=2.8 nm) trace of cubic Bi + trace of Bi_2Pt	supersaturated solid solution of FePt (a=0.3770 nm) + trace of Bi_2Pt trace of rhomb Bi
$Fe_{80}Pt_{11}Bi_9$ (3)	150	780 K	NCP of FePt (L=2.2 nm) + trace of Bi_2Pt + trace of FeO	supersaturated solid solution of FePt (a=0.3724 nm) + rhomb Bi (a=0.4679 nm; c=11.37 nm) + trace of Bi_2Pt + trace of FeO
$Fe_{85}Pt_6Bi_9$ (4) (5)	120 65	770 K	NCP of FePt (L=2.1` nm) + trace of Bi_2Pt	fcc FePt (a=0.3707 nm) + rhomb Bi (a=0.4680 nm; c=11.36 nm) + trace of FeO

where: d – thicknesses of film; NCP - nanocrystalline phase; romb Bi - equilibrium rhombohedral Bi phase, cubic Bi - non-equilibrium cubic Bi phase, L - coherent scattering region size (CSR).

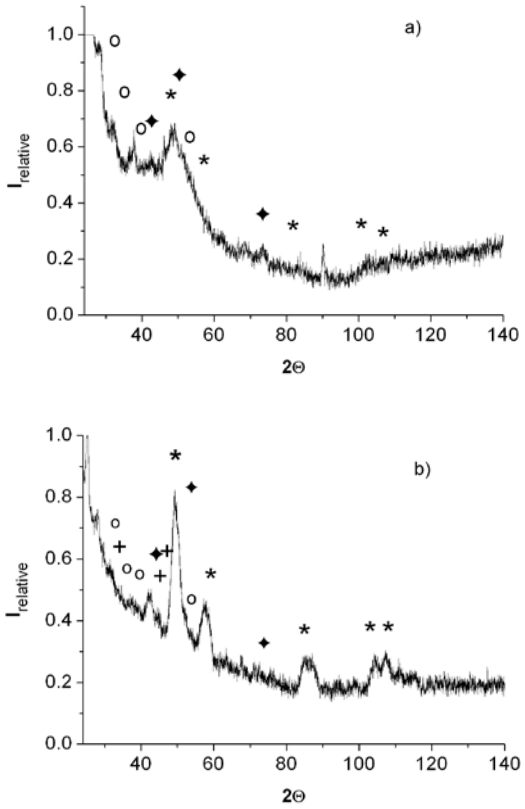

Fig. 1. X-ray diffraction patterns of $Fe_{80}Pt_{11}Bi_9$ films: a) in initial state; b) after heat treatment, where; + - Bi rhombohedral; Δ - Bi cubic; * – nanocrystalline FePt phase (NCP); * – fcc; ♦ – FeO

The first section (from 295 K to 550 K) in the Fe-Pt-Bi films is characterized by a reversible change in resistance. This indicates that in this temperature range phase transitions does not occur and the sample structure remains stable. The second area is characterized by an irreversible decrease in the surface resistance in the temperature range from 550 K to 690 K, which indicates the phase transitions and changes in the film structure associated with recrystallization processes. At a temperature of ~800 K, the sample is subjected to strong oxidation. The third region is characterized by a reversible decrease in resistance during cooling from 770 K to 440 K. There is a instant increase in resistance (two fold) due to the Bi crystallization by lowering the sample temperature to ~ 440 K. The most typical temperature dependence of the surface resistance is shown in Fig. 2. The Fe-Pt-Bi films (composition 3-5) are characterized precision value of temperature coefficient of resistance $3\text{-}6\times10^{-5}$ K^{-1} in initial state.

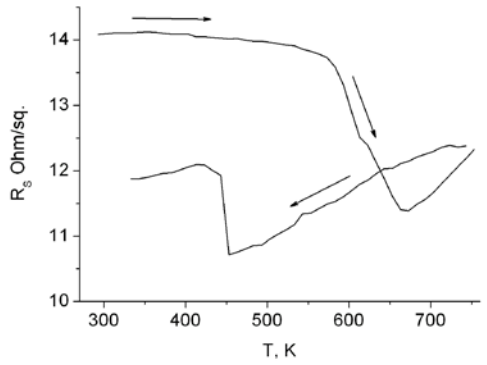

Fig. 2. The temperature dependence of the resistivity of $Fe_{80}Pt_{11}Bi_9$ film

As a result of the phase transition temperature displacement investigations with the increase in the heating rate there are the calculation of the activation energy of phase transformations (E_A) by Kissinger method. The Fe-Pt-Bi films activation energy is in the range E_A~7 - 13×10^3 K, depending on the film thickness and phase composition. The demagnetization curves analysis (Fig. 3) of the FePtBi (composition 1-2) films did not show hysteresis characteristics in parallel and perpendicular fields.

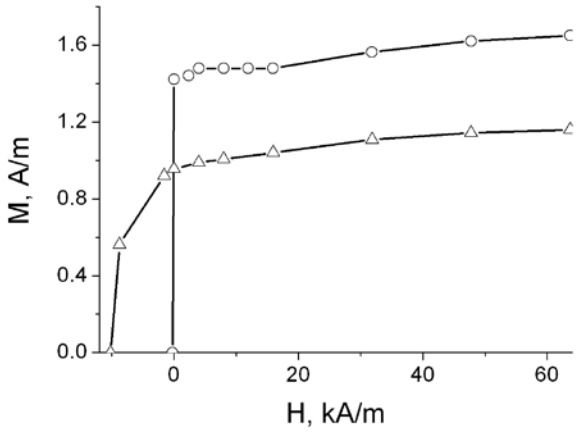

Fig. 3. Demagnetization curve of the film after heat treatment: ° – Fe (*d*=80 нм) Δ - $Fe_{85}Pt_6Bi_9$

The FePtBi films (composition 3-4) are characterized by anisotropy of magnetic properties. In the perpendicular magnetic field orientation, the films are showing the weak hysteresis properties. The coercivity does not exceed 0.16 kA/m in the initial state in parallel fields. Heat treatment at 770 K results in increasing coercivity up to 11 kA/m.

Heating above this temperature leads to the oxidation, which leads to significant deterioration of magnetic properties. Thus, improvement of magnetic characteristics can be realized by choosing holding time at a predetermined temperature.

4. Conclusions

The nanocrystalline phase (NCP) formation of the Fe-Bi-Pt films is determined by using the X-ray analysis. The decomposition of NCP after heat treatment and formation supersaturated solid solution of FePt leads to an increase in coercivity up to 11 kA/m. The $Fe_{80}Pt_{11}Bi_9$ and $Fe_{85}Pt_6Bi_9$ films are characterized precision value of temperature coefficient of resistance $3\text{-}6\times10^{-5}$ K^{-1} in the initial state.

References

1. **Congmian Zhen.** Effects of C layer on the microstructure and magnetic properties of FePt recording media films/ Congmian Zhen, Xiaoxia Zhai, Li Ma, Xiuling Li, Xiangfu Nie// Materials Science and Engineering B 129, 2006, p. –261–264

2. **Рябцев С.И.** Фазовый состав и свойства пленок на основе системы Fe-Bi/ С.И. Рябцев, В.Ф. Башев, Ф.Ф. Доценко, А.С. Рябцев// Вісник Дніпропетровського університету. Фізика. Радіоелектроніка. –2006, випуск 13, №2/3, - с.98-101

3. **Рябцев С.И.** Особенности фазообразования и свойства неравновесно закристаллизованных пленок системы Fe-Pt/ С.И. Рябцев, В.Ф. Башев, П.С. Гусевик, Ф.Ф. Доценко// Вісник Дніпропетровсько го університету. Серія Фізика. Радіоелектроніка - 2012, Випуск 19, №2, т.20, –с. 72-76

4. **Martin P.M.** Handbook of deposition technologies for films and coatings 3rd edition // Elsevier, –2010, p. – 912.

5. **Bashev V.F.** Structure and Electrical Properties of Ag–W Films in Metestable States. / V.F Bashev, F.F. Dotshenko, I.S. Miroshnichenko, V.H. Pasalsky// The Physics of Metals and Metallography, –1992, Vol. –73, No 2, P. – 152-156

6. **Grant W.A.** Preparation of amorphous alloys by ion implantation / W.A. Grant, A. Ali, L.T. Chadderton, P.J. Grundy// London: Third international conference of rapidly quenched metals, –1978.

7. **Kissinger H.E.** Variation of peak temperature with heat-ing rate // J. Res. Nat. Bur. Stand, –1956, Vol. 57, No 4. – P. 217 – 220.

Received 15.05.2015