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## STRUCTURE AND PROPERTIES OF PURE Mn, Bi AND MnBi FILMS IN METASTABLE STATE

The regularities of formation of Bi, Mn and MnBi metastable film structures obtained by modified three-electrode ion-plasma sputtering method (IPS) were researched. X-ray analysis shown that in the as-deposited Bi films a mixture of rhombohedral Bi phase ( $L = 6.5$  nm) with traces of cubic Bi was formed. Heat treatment led to the enlargement of the grains and the complete disappearance of Bi with a cubic lattice. MnBi films were a mixture of rhombohedral Bi phase and  $\beta$ -Mn in the initial state. After heat treatment, traces of  $\text{Bi}_2\text{Mn}$  and MnO appeared besides those phases. The analysis of the temperature dependence of resistivity revealed that for pure Mn, Bi and MnBi the activation energies of the phase transitions were  $E_A \sim 5000$  K,  $E_A \sim 8500$  K and  $E_A \sim 3500$  K respectively. After heating the Bi and MnBi films to the temperatures above 670 K and subsequently cooling them to a temperature of 490 K there was an abrupt change in resistance. The analysis of demagnetization curves showed that the hysteresis of magnetization was observed only in the films containing Bi because of the assumed manifestations of ferrimagnetic properties of Bi oxide in the non-equilibrium state.

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

В работе исследованы закономерности формирования метастабильных структур пленок Bi, Mn и MnBi полученных модернизированным методом трехэлектродного ионно-плазменного распыления (ИПР). В результате рентгеноструктурного анализа установлено, что в свеженанесенных пленках чистого Bi образуется смесь фаз ромбоэдрического Bi ( $L=6.5$  нм) и следов кубического Bi. Термообработка приводила к укрупнению зерен и полному исчезновению Bi с кубической решеткой. Пленки MnBi в исходном состоянии представляли смесь фаз ромбоэдрического Bi и  $\beta$ -Mn. После термообработки кроме указанных фаз появлялись следы  $\text{Bi}_2\text{Mn}$  и MnO. Анализ кривых температурной зависимости электросопротивления пленок позволил установить, что для чистых Mn, Bi и MnBi энергия активации фазовых переходов составляет  $E_A \sim 5000$  К,  $E_A \sim 8500$  К и  $E_A \sim 3500$  К соответственно. При нагреве пленок чистого Bi и MnBi до температуры выше 670 К и последующем охлаждении до температуры 490 К происходило скачкообразное изменение сопротивления. Анализ кривых размагничивания пленок показал, что гистерезис намагничивания наблюдается только в пленках содержащих Bi, поскольку предполагается проявление ферримагнитных свойств оксида Bi в неравновесном состоянии.

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

У роботі досліджені закономірності формування метастабільних структур плівок Bi, Mn, та MnBi отриманих модернізованим методом трьохелектродного іонно-плазмового розпилювання (ИПР). В результаті рентгеноструктурного аналізу встановлено, що в свіженанесених плівках чистого Bi утворюється суміш фаз ромбоэдричного Bi ( $L=6.5$  нм) та слідів кубічного Bi. Термообробка приводила до збільшення зерен та повного зникнення Bi з кубічною решіткою. Плівки MnBi в початковому стані являли суміш фаз ромбоэдричного Bi та  $\beta$ -Mn. Після термообробки крім зазначених фаз з'являлись сліди  $\text{Bi}_2\text{Mn}$  та MnO. Аналіз кривих температурної залежності електроопору плівок дозволив встановити, що для чистих Mn, Bi та MnBi енергія активації фазових переходів складає  $E_A \sim 5000$  К,  $E_A \sim 8500$  К та  $E_A \sim 3500$  К відповідно. При нагріві плівок чистого Bi та MnBi до температури більше 670 К та подальшому охолодженню до температури 490 К відбувалась стрибкоподібна зміна електроопору. Аналіз кривих розмагнічування плівок показав, що гістерезис намагнічування спостерігається тільки в плівках, які містять Bi, оскільки припускається наявність ферримагнітних властивостей оксиду Bi у нерівноважному стані.

**Ключові слова:** плівки MnBi, іонно-плазмове розпилювання, магнітотверді матеріали, метастабільний стан.

## Introduction

Significant interest in studying of MnBi alloys is due to the manifestation of high coercivity and residual magnetization, which is typical for high magnetic materials [1]. The MnBi ferromagnetic phase presence allows using this material as magnetic elements for microelectronic devices and high-density information recording [2]. Recently research has been carried out to improve 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. Such effects have a direct impact on the physical properties of samples. The paper investigates the structure, phase composition and physical properties of the Mn, Bi and MnBi films, as well as the influence of the deposition conditions and heat treatment on the original structure and properties.

## Materials and methods

Investigations were carried out on pure Mn, Bi and MnBi thin films with compositions (atomic %): Mn<sub>59</sub>Bi<sub>41</sub>; Mn<sub>56</sub>Bi<sub>44</sub>; Mn<sub>49</sub>Bi<sub>51</sub>; Mn<sub>42</sub>Bi<sub>58</sub>. The films with thicknesses about  $d \sim 150 - 400$  nm was obtained by a modernized three-electrode ion-plasma sputtering [3] under various deposition conditions (Table 1). The effective cooling rate for this method is theoretically estimated as  $10^{12} - 10^{14}$  K/s [4] and associated with the relaxation of individual atoms on the substrate. Inert Ar was used as the working gas. The film thickness was determined by the gravimetric method through weighing the substrate before and after spraying.

Table 1

Conditions of thin film deposition

	Mn	Bi	Mn+41%Bi	Mn+44%Bi	Mn+51%Bi	Mn+58%Bi
d, nm	160	500	380	240	340	150
I <sub>A</sub> , A	1	1	0.8	2	0.8	0.8
P <sub>Ar</sub> , mPa	120	120	16	53	16	16
U, kV	-2	-2	-2	-2	-2	-2
φ, eV	20	20	200	100	200	200

where U - target voltage; I<sub>A</sub> - anode current; P<sub>Ar</sub> - working gas pressure (Ar); d - film thickness; φ - the kinetic energy of the deposited atoms.

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 investigation 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 by the quadratic equations with an accuracy of  $\pm 0.001$  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  $\sim 10$  mPa with controlled heating rates between 4 and 20 K/min. The activation energy calculation of phase transitions was

performed by the Kissinger method, i.e. by analyzing the phase transition temperature displacement with heating rate changing. The film coercive force  $H_c$  was investigated by the vibration magnetometer in the maximum magnetizing field about 0.5 T, with parallel and perpendicular orientation to the film surface.

### Results and discussion

X-ray analysis results of the initial and heat-treated films are shown in Table 2. Investigations were performed on freshly deposited and heat-treated films with different thicknesses and obtained at different deposition conditions for studying the structure formation (for example, at reduced plasma gas pressure (from 120 to 16 mPa), which increases the energy of deposited atoms).

Table 2

Freshly deposited and heat-treated films phase composition

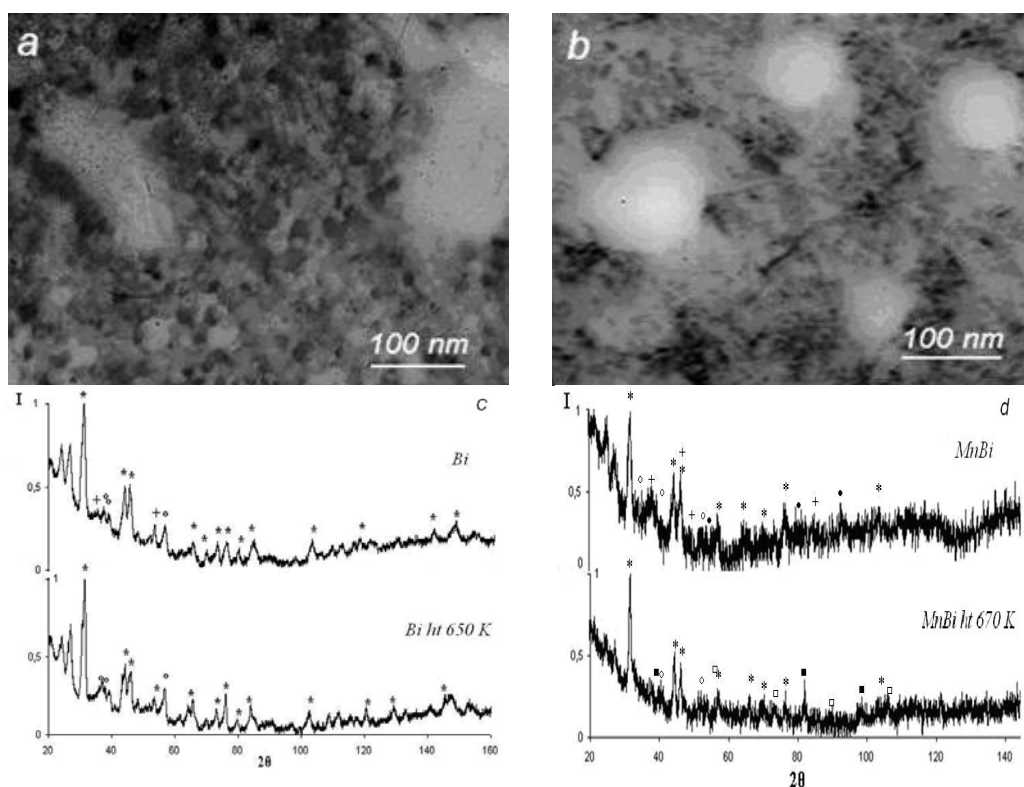
Composition (at.%)	Phase composition of films		
	The annealing temperature	In initial state	After heat treatment
Mn	770 K	$\beta$ -Mn ( $L=7.4$ nm) ( $a=0.688$ nm)	$\beta$ -Mn ( $L=10.5$ nm) ( $a=0.69$ nm) + MnO
Bi	650 K	rhomb Bi ( $L=6.5$ nm) ( $a=0.4552$ nm; $c=11.83$ nm) + cubic Bi + $\text{Bi}_2\text{O}_3$	rhomb Bi ( $L=8$ nm) ( $a=0.4515$ nm; $c=11.99$ nm) + $\text{Bi}_2\text{O}_3$
Mn+41%Bi	670 K	rhomb Bi ( $L=7$ nm) ( $a=0.4543$ nm; $c=11.84$ nm) + cubic Bi + $\beta$ -Mn ( $a=0.6985$ nm)	rhomb Bi ( $L=9$ nm) ( $a=0.4679$ nm; $c=11.37$ nm) + $\text{Bi}_2\text{Mn}$ + $\beta$ -Mn ( $a=0.703$ nm) + MnO
Mn+44%Bi	660 K	rhomb Bi ( $L=6.7$ nm) ( $a=0.462$ nm; $c=11.8$ nm) + cubic Bi + $\beta$ -Mn ( $a=0.632$ nm)	rhomb Bi ( $L=8$ nm) ( $a=0.452$ nm; $c=11.22$ nm) + $\beta$ -Mn ( $a=0.697$ nm) + MnO
Mn+51%Bi	690 K	rhomb Bi ( $L=6.5$ nm) ( $a=0.4533$ nm; $c=12.08$ nm) + cubic Bi + $\beta$ -Mn ( $a=0.6292$ nm)	rhomb Bi ( $L=13$ nm) ( $a=0.4552$ nm; $c=11.85$ nm) + $\text{Bi}_2\text{Mn}$ + $\beta$ -Mn ( $a=0.633$ nm) + MnO
Mn+58%Bi	670 K	rhomb Bi ( $L=9.5$ nm) ( $a=0.39$ nm; $c=11.91$ nm) + cubic Bi + $\beta$ -Mn ( $a=0.6249$ nm)	rhomb Bi ( $L=11$ nm) ( $a=0.4538$ nm; $c=12.05$ nm) + $\beta$ -Mn ( $a=0.6328$ nm) + MnO

where rhomb Bi - equilibrium rhombohedral Bi phase, cubic Bi - non-equilibrium cubic Bi phase, L - coherent scattering region size (CSR).

In the initial Mn films the nanocrystalline  $\beta$ -Mn phase (with CSR size  $L \sim 7.4$  nm) was observed. After heat treatment in vacuum at a temperature of 770 K manganese is oxidized with the MnO oxide formation, and CSR size of  $\beta$ -Mn phase increases to 10.5 nm.

In the original Bi films there were the mixture of equilibrium rhombohedral Bi phase (with the CSR size  $L \sim 6,5$  nm), nonequilibrium Bi with a cubic lattice, and traces of  $\text{Bi}_2\text{O}_3$  oxide (Fig. 1c). The heat treatment of the films at a temperature of  $\sim 650$  K leads to the decay of Bi cubic and its transition to the equilibrium state, and there is an increase of the CSR size of Bi rhombohedral to  $L \sim 8$  nm. The structure of initial Bi film is shown in Fig. 1a.

In the MnBi films, as shown by electron diffraction and X-ray studies, in the initial state there were a mixture of the cubic and rhombohedral Bi phases as well as  $\beta$ -Mn traces. The CSR sizes of rhombohedral Bi phase for various compositions are shown in Table 2 and are in the range of  $L \sim 6.5 - 9.5$  nm. After heat treatment at temperatures of 670 K there was a grain growth of rhombohedral Bi phase ( $L \sim 8 - 13$  nm) and the change of the lattice to the values corresponding to the equilibrium state (Fig. 1d). As in the case of heat treatment of pure Mn and Bi, there were the decay of nonequilibrium Bi and  $\beta$ -Mn phase oxidation. Furthermore, in the  $\text{Mn}_{59}\text{Bi}_{41}$  and  $\text{Mn}_{49}\text{Bi}_{51}$  films obtained with the low



**Fig. 1. X-ray diffraction patterns and microstructure of Bi and MnBi films: a) the structure of the original Bi film; b) the structure of the original  $Mn_{49}Bi_{51}$  film; c) X-ray patterns of Bi film in initial and heat-treated states; d) X-ray patterns of  $Mn_{49}Bi_{51}$  film where; \* - Bi rhombohedral; + - Bi cubic;  $^{\circ}$  -  $Bi_2O_3$ ;  $\bullet$  -  $\beta$ -Mn;  $\blacksquare$  -  $Bi_2Mn$ ;  $\square$  - MnO.**

pressure of working gas and the high energy of deposited atoms, after heat treatment there was intermediate  $Bi_2Mn$  phase formation. In the  $Mn_{42}Bi_{58}$  film obtained under identical conditions the formation of the intermediate phase does not occur; this may be due to the relatively low film thickness (150 nm). The typical structure of MnBi film is illustrated in Fig. 1b. On the X-ray and electron diffraction there is broadening of the diffraction peaks, which may be associated with the occurrence of internal stresses during the formation of an intermediate phase.

The thermal stability of the films was investigated by recording the temperature dependence of the surface resistivity in a vacuum at a constant heating rate. The temperature dependence of the resistance curves are characterized by a number of characteristic sections.

In the pure Mn films the first section (from 295 K to 600 K) 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 620 K to 700 K, which indicates the phase transitions and changes in the film structure associated with recrystallization processes. At a temperature of  $\sim 800$  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 295 K.

In the MnBi films the first section is in the temperature range from 295 K to 570 K. The second section, showing a phase transition, is about from 570 K to 670 K, and the third temperature region is about from 700 K to the room temperature.

The Bi resistivity behavior during heating and cooling is different from the described above areas. At a temperature of 620 K there is a phase transition associated with the Bi melting, which is manifested in a relatively sharp decrease in resistance. The resulting melting point of Bi film is different from the data on the melting point of bulk samples by about 60 K. There is an instant increase in resistance (two fold) due to the Bi crystallization by lowering the sample temperature to  $\sim 480$  K. The most typical temperature dependence of the surface resistance is shown in Fig. 2.

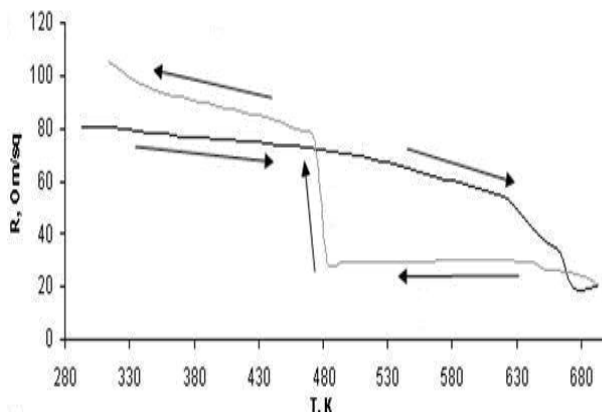


Fig. 2. The temperature dependence of the resistivity of Bi film.

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 the Kissinger method. In pure Mn and Bi films the activation energy is  $E_A \sim 5 \times 10^3$  K and  $E_A \sim 8.5 \times 10^3$  K. The MnBi films activation energy is in the range  $E_A \sim 3 - 5 \times 10^3$  K, depending on the film thickness and phase composition.

The demagnetization curve analysis of the pure Mn films, as expected, did not show hysteresis characteristics in parallel and perpendicular fields. In Bi films the hysteresis properties are manifested due to the formation  $\text{Bi}_2\text{O}_3$  oxide as a result, so the magnetic moment of the sample is uncompensated. MnBi films are characterized by anisotropy of magnetic properties. In the perpendicular magnetic field the films show the weak hysteresis properties. The coercivity does not exceed 2 kA/m in the initial state. Heat treatment at 720 K leads to an increase in coercivity up to 38 kA/m (Fig. 3). Heating above this temperature leads to the Mn oxidation, which leads to significant deterioration of magnetic properties. Thus, improvement of magnetic characteristics can be realized by choosing the exposure time at a predetermined temperature.

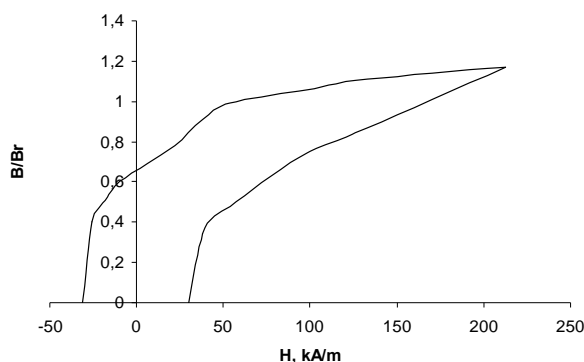


Fig. 3. Demagnetization curve of the  $\text{Mn}_{49}\text{Bi}_{51}$  alloy after heat treatment

### Conclusions

As a result, we can say that with the X-ray analysis and investigation of the magnetic properties of the Bi films was determined  $\text{Bi}_2\text{O}_3$  oxide formation, which contributes to the manifestation of the hysteresis properties. The investigation of the deposition condition influence on the film structure has shown that the intermediate  $\text{Bi}_2\text{Mn}$  ferromagnetic phase is formed in the case of reduced pressure of the working gas and relatively high energy of the deposited atoms. The melting point of Bi films produced under non-equilibrium conditions is shifted by  $\sim 60$  K compared to the bulk samples. Our investigation of the samples temperature stability has shown that the heating of the MnBi films to the temperature above 750 K leads to the active Mn oxidation that results in significant deterioration of the electrical and magnetic characteristics.

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