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STRUCTURE AND PHYSICAL PROPERTIES OF Mn, Bi, MnBi AND MnBiCr FILMS OBTAINED BY ION-PLASMA SPUTTERING

The regularities of formation of Bi, Mn, MnBi, and MnBiCr metastable film structures obtained by modified three-electrode ion-plasma sputtering method are investigated. X-ray analysis shows that in the fresh sputtered Mn films a mixture of β-Mn (the size of coherent scattering region L = 7.5 nm) and oxide MnO is formed. Initial Bi film is a mixture of rhombohedral Bi phase (L = 6.5 nm) and traces of metastable bcc-Bi. Heat treatment leads to the enlargement of the grains and the complete disappearance of bcc-Bi. MnBi films are a mixture of rhombohedral Bi phase and β-Mn in the initial state. After heat treatment, besides those phases traces of Bi_2Mn and MnO appear. Addition of the barrier component of Cr prevents the formation of oxide MnO in the film. The activation energy of MnBi films are in the range of E_A ~ 3500 - 5000 K. After heating the Bi and MnBi films above 670 K and subsequently cooling to the temperature of 490 K there is an abrupt change in resistance. The analysis of the demagnetization curves shows that the hard magnetic properties are observed only in films containing the Bi_2O_3 phase.

Keywords: MnBi films, ion-plasma sputtering, hard magnetic materials, metastable state, temperature coefficient of resistance.

Досліджено закономірності формування метастабільних структур плівок Bi, Mn, MnBi та MnBiCr, отриманих модернізованим методом трьохелектродного іонно-плазмового розпилювання. За результатами рентгенофазового аналізу у свіжонапилених плівках чистого Mn утворюється суміш β-Mn (розмір області когерентного розсіювання L = 7,5 нм) та оксиду MnO. В плівках Bi утворюється суміш фаз ромбоедричного Bi (L=6.5 нм) та слідів метастабільного ОЦК-Bi. Термообробка призводить до збільшення зерен та повного розпаду ОЦК-Bi. Плівки MnBi в початковому стані представляють суміш фаз ромбоедричного Bi та β-Mn. Після термообробки крім зазначених фаз з'являються сліди Bi_2Mn та MnO. Додавання до складу плівок бар'єрного Cr перешкоджає утворенню оксиду MnO. При нагріві плівок чистого Bi та MnBi вище 670 К та подальшому охолодженні до температури 490 К відбувається стрибкоподібна зміна електроопору. Аналіз кривих розмагнічування плівок показав, що магнітотверді властивості спостерігаються тільки в плівках, які містять фазу Bi_2O_3.

Ключові слова: плівки MnBi, іонно-плазмове розпилювання, магнітотверді матеріалі, метастабільній стан, температурний коефіцієнт електроопору.

Исследованы закономерности формирования метастабильных структур пленок Bi, Mn, MnBi и MnBiCr, полученных модернизированным методом трехэлектродного ионно-плазменного распыления. По результатам рентгенофазового анализа в свеженапыленных пленках Mn образуется смесь фаз β-Mn (размер области когерентного рассеяния L = 7,5 нм) и оксида MnO. В исходных пленках Bi образуется смесь фаз ромбоэдрического Bi (L = 6,5 нм) и следов метастабильного ОЦК-Bi. Термообработка приводит к укрупнению зерен и полному распаду ОЦК-Bi. Пленки MnBi в исходном состоянии представляют смесь фаз ромбоэдрического Bi и β-Mn. После термообработки кроме указанных фаз появляются следы Bi_2Mn и MnO. Добавление в состав пленок барьерного Cr препятствует образованию оксида MnO. При нагреве пленок чистого Bi и MnBi выше 670 К и последующем охлаждении до температуры 490 К происходит скачкообразное изменение сопротивления. Анализ кривых размагничивания пленок показал, что магнитотвердые свойства наблюдаются только в пленках, содержащих фазу Bi_2O_3.

Ключевые слова: пленки MnBi, ионно-плазменное распыление, магнитотвердые материалы, метастабильное состояние, температурный коэффициент электросопротивления.

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1. Introduction

Bulk materials based on MnBi system with a certain proportion of the low-temperature ferromagnetic MnBi phase are widely known for their magnetic properties and used in plastic magnets [1]. Preparation of such magnetic material in the film form was of special interest. Films based on MnBi can give any form and sizes. There are main advantages of films over bulk materials.

Because of oxidation in air, the significant deterioration of magnetic characteristics of MnBi film was manifested. In thin films, the contents of ferromagnetic MnBi phase could be significantly reduced due to MnO formation. In most cases the layering deposition is applied as protective coating to prevent the magnetic film oxidation. Also, you can use an additional component, which prevents the oxidation and may lead to a significant improvement of physical properties. Selection of such component was a major problem of this work.

In addition to the MnBi system, there is a well-known Bi-magnetic compound with chromium. The applications of this compound are limited by the specific technological areas due to the synthesis difficulties. Preparation of such compounds was possible under extremely non-technical conditions by physical vapor deposition (PVD)[2].

The chromium has a high melting point and CrO oxide prevents the further surface oxidation. This component reacted with a low-melting Bi and forms several intermediate phases with Mn. Moreover, chromium has similar magnetic properties with manganese. Even at relatively low temperatures, Mn and Cr are antiferromagnets.

In this work, the MnBi film structure and physical properties, temperature and corrosion resistance, and the influence of added chromium component are studied.

2. Materials and methods

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 investigated 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 ± 0.001 nm.

The physical properties and thermal stability were examined for the films deposited at pyroceramics substrates. The film surface resistivity was measured by the four-probe method with continuous heating in vacuum of 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 [3], by analyzing the phase transition temperature displacement with heating rate changing. The film coercive forces H_c were measured by a vibration magnetometer in the maximum magnetizing field about 0.5 T, with parallel and perpendicular orientation to the film surface.

In this paper, the objects of research were the Bi, Mn, MnBi and MnBiCr films. The compositions and deposition conditions are shown in Table 1. The film thicknesses were about 150-900 nm.

The film deposition was performed by the modernized ion-plasma sputtering PVD in vacuum. The targets were placed directly on the sputtered surface of certain component parallelepipeds [4]. The effective cooling rate was estimated as 10^{12}-10^{14} K/s and associated with the individual atoms relaxation time on the substrate [5].

3. Results and discussion

The transmission electron microscopy (TEM), XRD and CSR analysis showed: A) In freshly deposited Mn films there was a mixture of β-Mn nanocrystalline phase (CSR size L ~ 7.4 nm) and MnO oxide. The significant Mn oxidation and MnO formation were observed under heat treatment in vacuum at the temperature about 770 K.

Table 1

Conditions of thin film deposition

Film compositions	d, nm	I_A, A	P_{Ar}, mPa	U, kV	φ, (eV)
Mn	1000	2	53	-2	100
Mn	160	1	120	-2	20
Bi	900	0.8	16	-2	200
Bi	500	1	120	-2	20
$Mn_{59}Bi_{41}$	380	0.8	16	-2	200
$Mn_{56}Bi_{44}$	240	2	53	-2	100
$Mn_{49}Bi_{51}$	340	0.8	16	-2	200
$Mn_{49}Bi_{51}$*	880	2	53	-2	100
$Mn_{42}Bi_{58}$	150	0.8	16	-2	200
$Mn_{46}Bi_{17}Cr_{37}$	490	2	53	-2	100
$Mn_{63}Bi_{15}Cr_{22}$	360	1	120	-2	20
$Mn_{68}Bi_{25}Cr_{7}$	280	1	120	-2	20

Note: d – film thickness; I_A – anode current; P_{Ar} – working gas pressure (Ar);
U – target voltage; φ – the kinetic energy of the deposited atoms

B) In the original Bi films the mixture of Bi equilibrium with a rhombohedral lattice (L ~ 6.5 nm) and Bi non-equilibrium with a cubic lattice, as well as Bi_2O_3 phases were formed (Fig. 1a). The film heating to a temperature above the melting point (~770 K) and subsequent cooling lead to Bi transition to the equilibrium state and grain growth to ~8 nm.

C) The original MnBi films were the mixture of rhombohedral and cubic Bi phases and the β-Mn phase (Fig. 1b). In the rhombohedral Bi phase, the CSR sizes were L ~ 6.5-9.5 nm. This parameter depended on the deposition conditions and film thicknesses. When working gas pressure was increased and therefore the atom energy decreased, the CSR size of Bi phase was decreased too. However, when the film thickness was increased there was the opposite effect. The film heat treatment at a temperature about 670 K lead to the intermediate Bi_2Mn phase and MnO oxide formation. The Bi_2Mn phase was formed in films with higher contents of Mn than Bi. The nonequilibrium phase of Bi with a cubic lattice was stabilized. The rhombohedral CSR size of Bi increased to L ~ 11-13 nm.

D) In the initial MnBiCr films rhombohedral Bi phase (L ~ 7 nm) as well as Bi traces and β-Mn cubic phases were detected. Cr was in a solid solution as evidenced by the Bi lattice parameter change (a/c = 0.32). After heat treatment at about 710 K the Bi lattice parameter approached to the tabulated values (a/c = 0.4). There was an increase of the rhombohedral CSR size of Bi to L ~ 8-9 nm. In addition, there were traces of CrO oxide. In contrast to MnBi films without Cr, in the MnBiCr film Mn oxidation was not observed.

Investigations of film temperature dependences of resistivity during heating and cooling showed that the curves could be divided into five main sections (Fig. 2). At the first stage, the heating of Bi films to about 550 K leads to a gradual decrease in resistivity. At the second stage, depending on the composition and the heating rate, there was a sharp decline in resistance, which displays the recrystallization and phase transition processes. Upon further cooling, electrical resistivity remains constant up to a certain temperature (~ 480 K).

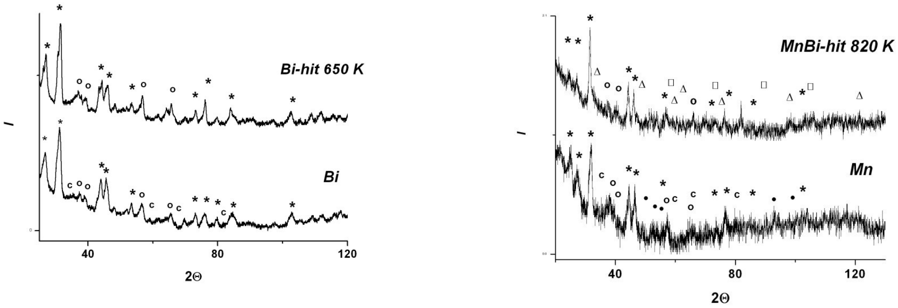

Fig. 1. X-ray diffraction patterns of Bi and MnBi films: a) X-ray patterns of Bi film in initial and heat-treated states; b) X-ray patterns of $Mn_{49}Bi_{51}$ film
where: * - Bi rhombohedral; c - Bi cubic; o – Bi_2O_3; • - β-Mn; Δ – Bi_2Mn; □ – MnO.

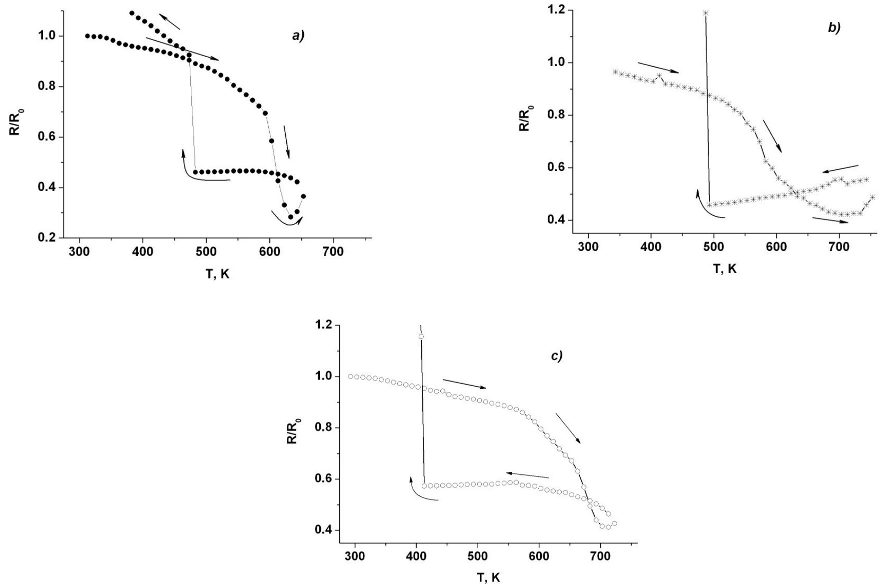

Fig. 2. Temperature dependences of the resistivity of Bi (a); Mn51Bi (b); Mn25Bi7Cr (c) at the heating rate 9 K/min.

In this area, there was almost doubled sharp increase in resistance. For the Bi and MnBi films this temperature was about 490 K, and for MnBiCr – about 440 K. There was a further increase in electrical resistance at the last step.

When the films were heated to a temperature below 670 K and then cooled, there was no sharp change in resistance. This temperature was comparable to the Bi phase transition temperature to a liquid phase. These melting point data of Bi thin films are different from literature values for the bulk samples by 40 - 80 K. In a series of repeated film heating and cooling cycles, there was a regular resistivity behavior (Fig. 3).

The film phase changes with heating rate increasing allowed us to calculate the activation energy of the phase transitions (E_A). For pure Mn and Bi films activation energy were E_A~5×10^3 K and E_A~8.5×10^3 K. The activation energy of the MnBi films were in the range E_A~3.5-5×10^3 K, depending on the thickness and phase composition. In MnBiCr films there were two bending curves of the temperature dependence of the resistivity. The first curve, at a temperature of 573 K was associated with Bi melting (E_A~7-8×10^3 K), and the second one was related to recrystallization processes at ~653 K (E_A~5.2×10^3 K).

The demagnetization curves analysis of pure Mn films showed the absence of hysteresis properties, in a parallel and perpendicular fields. Pure Bi, as we know, is a diamagnetic, but in the studies of magnetic properties of the film samples there were manifestation of hysteresis properties (H_c ~ 16 kA/m).

As we know from our studies of magnetic properties of the Bi-oxygen compounds [6], for the α-Bi_2O_3 phase there was streamlining internal magnetic fields, as well as the paramagnetic properties. In our case, the Bi structure has two sublattices (rhombohedral and cubic), which correspond to the equilibrium and nonequilibrium Bi states and their oxides Bi_2O_3. Thus, magnetic moments were uncompensated, which is typical for ferrimagnets.

MnBi films showed anisotropic magnetic properties. In the initial state, the coercivity was not greater than 2 kA/m. Heat treatment at 720 K leads to an increase in coercivity in a parallel field up to 38 kA/m (Fig. 4).

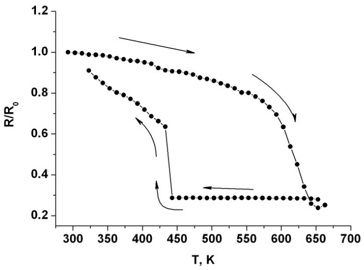

Fig. 3. The temperature dependence of the resistivity of the Mn25Bi7Cr film.

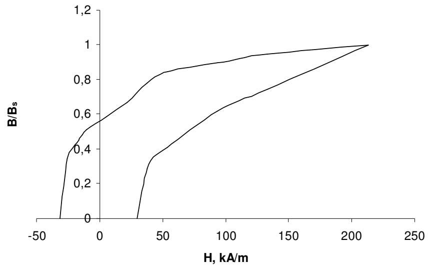

Fig. 4. Demagnetization curves of $Mn_{49}Bi_{51}$ films after heat treatment (710 K).

Further coercivity increasing can be achieved by adjusting the delay time depending on the original films composition. In the MnBi films at a temperature above 720 K there was an active Mn oxidation, which leads to significant deterioration of magnetic characteristics. The Cr addition leads to a hindering the oxidation process, thus allowing to increase the films thermal stability. In a parallel field the original MnBiCr film coercivity was H_c ~ 15 kA/m. Further heat treatment at temperatures about 620 – 780 K does not lead to a significant change in magnetic properties. Thus, Cr adding allows us to increase the temperature range in which the films retain their magnetic characteristics.

For calculating the elastic stress of the metal films, which arise due to the difference of thermal expansion coefficients of the film and substrate, the model of the approximation of a two-layer structure for semiconductor films [7] was used. As can be seen in the figure (Fig. 5), the mechanical stress values take opposite signs on different substrates. With using the obtained data, it was found that the formation of non-equilibrium Bi phase, which is formed, as noted, only at high pressure, can be explained by the high cooling rate and high mechanical stress levels between the film and the substrate (σ ~ 0.3 – 0.4 MPa).

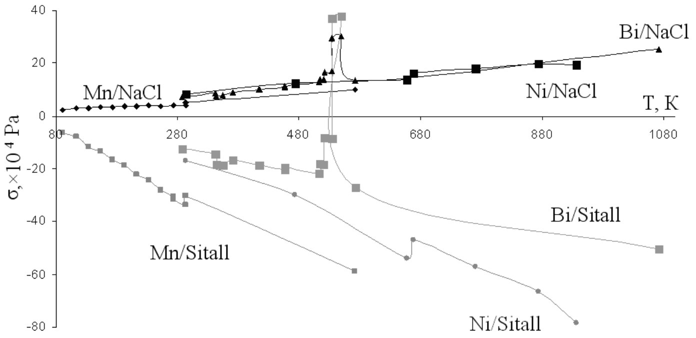

Fig. 5. Temperature dependence of mechanical stresses.

Thus, an increased deposited atoms energy level (~ 200 eV) during the Bi films deposition and elastic mechanical stress lead to the formation of a metastable Bi phase at atmospheric pressure.

5. Conclusions

With using the methods of X-ray diffraction, electron microscopy, and construction of the temperature dependence of electrical resistivity and demagnetization curves, the structure and physical properties of MnBi films and the Cr addition effect were studied. As a result, it should be noted that the Bi films showed the hysteresis properties through the formation of Bi oxide sublattices with a non-equilibrium structure. An uncompensated total magnetic moment of the equilibrium and non-equilibrium Bi oxides leads to the emergence of ferromagnetic properties. The investigation of the temperature dependence of the resistance showed that Bi crystallization temperature, which was manifested as a sharp increase of resistance, was the same for pure Bi and MnBi films (490 K), but in the MnBiCr films this temperature was greatly reduced (430 K). As a result of annealing the MnBi films at a temperature of 710 K, coercivity was about 38 kA/m and can be increased by adjusting a delay time.

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