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Magnetic and Structure Properties of CoPt-In_2O_3 Nanocomposite Films

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Abstract. The structural and magnetic properties of CoPt-In_2O_3 nanocomposite films formed by vacuum annealing of the In/(Co_3O_4 + Pt)/MgO film system in the temperature range of 100–800 °C have been investigated. The synthesized nanocomposite films contain ferromagnetic CoPt grains with an average size of 5 nm enclosed in an In_2O_3 matrix, and have a magnetization of 600 emu/cm^3, and a coercivity of 150 Oe at room temperature. The initiation 200 °C and finishing 800 °C temperatures of synthesis were determined, as well as the change in the phase composition of the In/(Co_3O_4 + Pt)/MgO film during vacuum annealing.

Keywords: thin films, ferromagnetic nanocomposites, CoPt alloy, In_2O_3 oxide.

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Introduction

In recent years, composite nanomaterials have been the subject of numerous studies due to their novel functional properties that differ from the properties of their components [1]. Composite ferromagnetic films containing nanoclusters of transition-metal Co, Fe, or Ni in a dielectric or semiconductor matrix obtained by different physical and chemical methods, including the sol-gel method, spray pyrolysis, the microemulsion method, magnetron sputtering, pulsed laser deposition, ion implantation, and joint deposition have been intensively studied [2–9]. The synthesis of these nanocomposites often passes under equilibrium conditions, but lately there has been a surge in nonequilibrium processing of ferromagnetic composites using methods like pulsed laser irradiation [10], pulsed laser deposition [11], ion implantation [12, 13], and the ball-milling process [14] and thermite synthesis of materials. Nanocomposites obtained under nonequilibrium

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conditions often have metastable phases and possess unusual magnetic and physicochemical properties. Recently, a simple and effective method of solid state synthesis of magnetic nanogranular thin films has been proposed, based on initiating thermite reactions between 3d-metal oxide films (Fe_2O_3, Co_3O_4) and In, Zr, Zn, Al metals, whose oxides are wide-gap semiconductors or dielectrics [15–19]. Such an approach makes it possible to obtain thin single-layer and multilayer nanogranular films with a well-controlled size and distribution of magnetic granules over the thickness of the film [19]. CoPt and FePt alloy films have attracted a great deal of attention because of their strong perpendicular magnetic anisotropy, which is important for many practical applications. To date, there have been a small number of studies on the synthesis and investigation of nanocomposites containing CoPt and FePt nanoparticles in oxide matrices [20–26]. These investigations are important for applications involving the synthesis of nanocomposites with the desired magnetic, structural, and transport properties.

In this work, we report the results of the synthesis and investigation of the structure and magnetic properties of CoPt-In_2O_3 nanocomposite films. The films were synthesized by a solid-state reaction in the In/(Co_3O_4 + Pt)/MgO film system with annealing in a vacuum at 10^{-6} Torr in the temperature range of 100 – 800 °C. The main synthesis parameters, including the initiation temperature and the phase composition of the reagents and reaction products, were determined.

Experimental procedures

Fig. 1 shows the scheme for synthesizing CoPt-In_2O_3 nanocomposite films. First, we prepared the CoPt(111) ferromagnetic films using the technique described in [20]. This began with the magnetron sputtering of Pt films with a thickness of ~ 50 nm in a vacuum at a residual pressure of 10^{-6} Torr onto a MgO(001) substrate heated to a temperature of ~ 250 °C, which ensured epitaxial growth of the Pt(111) plane relative to the substrate surface. Next was the thermal deposition of a polycrystalline Co film with a thickness of ~ 70 nm in a vacuum at a residual pressure of 10^{-6} Torr onto the Pt film at room temperature to prevent a reaction between the layers (the chosen thicknesses of the reacting layers were $\sim$70 nm for Co and ~ 50 nm for Pt, which provided an equiatomic composition), followed by the annealing of the obtained Co/Pt(111)/MgO bilayer samples in a vacuum at 10^{-6} Torr at a temperature of 650 °C for 90 min. After annealing the Co/Pt(111)/MgO samples, the magnetically hard L1_0-CoPt(111) phase forms in the Co/Pt(111) film structure based on the oriented Pt(111) layer [20, 27].

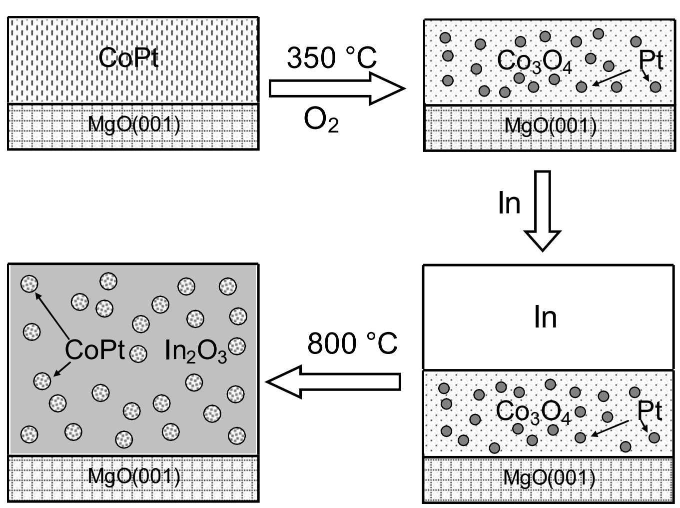

Fig. 1. Schematic of the formation of the CoPt-In_2O_3 nanocomposite films

Then, the $L1_0$-CoPt/MgO films were oxidized in air at a temperature of $\sim 350\,^\circ$C for 3 h. The oxidation yielded a Co_3O_4 + Pt film structure containing Pt nanoclusters dispersed in a Co_3O_4 matrix. It should be noted that in the method used, the Co was oxidized, while the Pt remained unoxidized.

The CoPt-In_2O_3 nanocomposite films were obtained by annealing the initial In/(Co_3O_4 + Pt)/MgO(001) samples in a vacuum at 10^{-6} Torr in the temperature range of $100-800\,^\circ$C with a step size of $100\,^\circ$C and exposure at each temperature for 40 min. Film magnetization was measured after each annealing. The formations of the Co and CoPt magnetic phases were detected by the occurrence of magnetization. Through these measurements, the temperatures of initiation and end of the CoPt-In_2O_3 nanocomposite synthesis were determined.

The thicknesses of the reacting layers were determined by X-ray fluorescence analysis. The saturation magnetization M_s was measured with a torque magnetometer in a maximum magnetic field of 17 kOe. Hysteresis loops in the CoPt-In_2O_3 film plane and perpendicular to it were measured on a vibrating sample magnetometer in magnetic fields up to 20 kOe. The phase composition was investigated by X-ray diffraction using a DRON-4-07 diffractometer in CuK_α radiation ($\alpha = 0.15418$ nm). The analysis of the intensity of the X-ray diffraction reflections were made using the ICDD PDF 4+ crystallographic database [28].

Results and discussion

Cobalt reduction and the formation of the CoPt ferromagnetic grains were investigated by measuring the saturation magnetization of the initial In/(Co_3O_4 + Pt)/MgO(001) samples as a function of the annealing temperature $M_s(T)$ (Fig. 2). It can be seen from the $M_s(T)$ dependence that, below $200\,^\circ$C, Co reduction processes do not occur in the investigated In/(Co_3O_4 + Pt) structure and its magnetization is therefore close to zero. The magnetization sharply increases at $T > 400\,^\circ$C and reaches a maximum at $T > 700\,^\circ$C. The $M_s(T)$ (Fig. 2) dependence includes three portions: near $T_1 \sim 200\,^\circ$C, near $T_2 \sim 400\,^\circ$C and near $T_3 \sim 700\,^\circ$C. It is well known [17] that T_1 is close to the temperature $\sim 200\,^\circ$C of Co reduction from the Co_3O_4 oxide in the In/Co_3O_4 film system. At the same time, it is well-known [27] that the $L1_0$-CoPt phase starts forming at a temperature of $\sim 375\,^\circ$C in Pt/Co films. We can conclude that, at $T_2 \sim 400\,^\circ$C, the reaction of the Co reduction from the Co_3O_4 oxide with the formation of the CoPt and In_2O_3 phases continues. At temperatures above $400\,^\circ$C, the magnetization of the film sharply grows, which indicates the continuation of the solid-state reaction in the In/(Co_3O_4 + Pt)/MgO(001) film with the formation of the CoPt and In_2O_3 phases. Annealing at $T > 700\,^\circ$C facilitates the occurrence of the maximum number of CoPt grains.

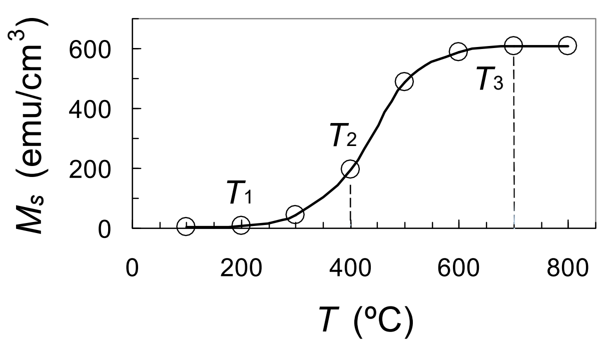

Fig. 2. Dependence of the saturation magnetization M_s on the annealing temperature T of the In/(Co_3O_4 + Pt)/MgO film

X-ray measurements performed after the oxidation of the $L1_0$-CoPt/MgO films in air at a temperature of ∼ 350 °C for 3 h and the deposition of the In layer showed that the obtained system consists of the Co_3O_4 (the space group Fd-3m, lattice constant a = 8.0837 Å, PDF Card # 00-042-1467), Pt (the space group Fm-3m, lattice constant a = 3.9231 Å, PDF Card # 00-004-0802), and In (the space group I4/mmm, lattice constants: a = 3.252 Å, c = 4.9466 Å, PDF Card # 04-004-7737) phases (Fig. 3 a). Annealing at a temperature of 400 °C (Fig. 3 b) led to the formation of a small amount of the ordered $L1_0$-CoPt tetragonal phase in the reaction products, which is confirmed by the presence of the (001) superstructural reflection (the space group P4/mmm, lattice constant a = 2.677 Å, c = 3.685 Å, PDF Card # 04-003-4871). The In_2O_3 reflections are also present in the diffraction pattern (the space group Ia-3, lattice constant a = 10.118 Å, PDF Card # 00-006-0416). When annealing at temperatures below 400 °C reflections from the reduced cobalt were not observed because of its high dispersion.

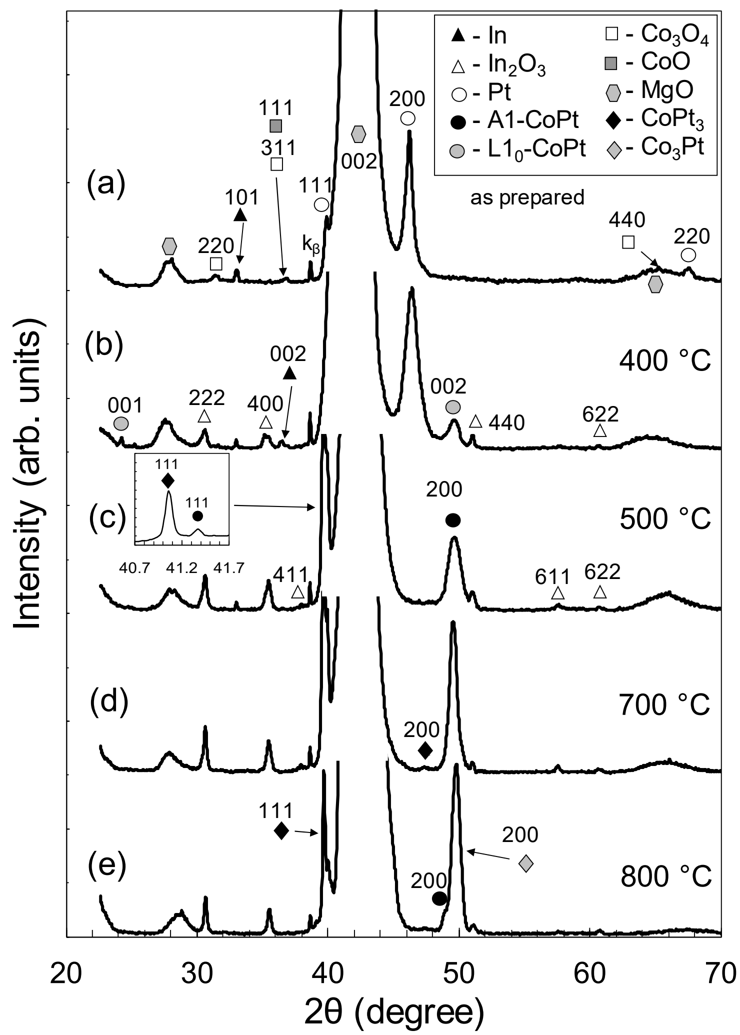

Fig. 3. X-ray diffraction patterns of the In/(Co_3O_4 + Pt)/MgO film after annealing in a vacuum in the temperature range of 100 – 800 °C

When the sample was heated to 500 °C (Fig. 3 c), the reflections from the Pt phase disappear and reflections from the disordered A1-CoPt (the space group Fm-3m, lattice constant a = 3.768 Å, PDF Card # 04-001-0115) and $CoPt_3$ (the space group Pm-3m, lattice constant a = 3.831 Å, PDF Card # 04-004-5243) phases appear. When the sample was annealed to 700 °C (Fig. 3 d), the intensity of the diffraction reflections increased, which is related to reaction relaxation processes, including the increase of the size of the CoPt grains and the improvement of the crystal quality in the insulating In_2O_3 matrix, but no new phases were formed. Annealing at $T = 800$ °C (Fig. 3 e) led to the formation of the Co_3Pt (the space group Fm-3m, lattice constant a = 3.668 Å, PDF Card # 01-071-7411) phase.

The CoPt grain size was estimated from the width of the Co_3Pt (200) reflections (Fig. 3 e) by the Scherrer formula $d = k\lambda/\beta\cos\theta$, where d is the mean crystal grain size, β is the diffraction maximum width measured at half the maximum, λ is the X-ray radiation wavelength (0.15418 nm), θ is the diffraction angle corresponding to the maximum of the peak, and $k = 0.9$. The obtained calculated size of the crystal grains of CoPt was $\sim$ 5 nm.

X-ray diffraction allows us to conclude that after annealing the film contains CoPt (A1-CoPt + $CoPt_3$ + Co_3Pt) alloy nanograins surrounded by In_2O_3. The synthesis of the nanocomposite includes the following successive solid-state reactions:

1. 200 °C → 8In + $3Co_3O_4$ = 9Co + $4In_2O_3$,
2. 400 °C → Co + Pt = $L1_0$-CoPt,
3. 500 - 700 °C → Co + Pt = A1-CoPt and A1-CoPt + 2Pt = $CoPt_3$,
4. 800 °C → A1-CoPt + 2Co = Co_3Pt.

When annealing above 400 °C, the transition of the cubic CoPt phase to the tetragonal $L1_0$-CoPt phase does not occur and the formed films are low-coercive. Recently, we synthesized high-coercive CoPt-Al_2O_3 films under the same synthesis conditions (an equiatomic composition Co:Pt = 50:50 on an MgO(001) substrate, vacuum annealing) [20, 27]. It's possible this difference between the synthesis of CoPt-In_2O_3 and CoPt-Al_2O_3 nanocomposite films is due to the fact that in In/(Co_3O_4 + Pt)/MgO(001) films the cobalt is restored before ($\sim$ 200 °C) the formation of the $L1_0$-CoPt phase ($\sim$ 400 °C) and the formed In_2O_3 phase prevents the transition of the cubic CoPt phase to the tetragonal $L1_0$-CoPt phase. In the synthesis of CoPt-Al_2O_3 films, in Al/(Co_3O_4 + Pt)/MgO(001) films, the formation of the $L1_0$-CoPt phase occurs at $\sim$ 375 °C and the Co is restored from the Co_3O_4 oxide at $\sim$ 490 °C [20, 27].

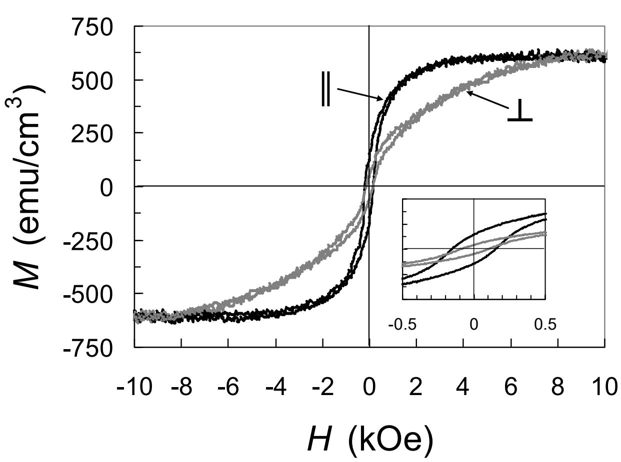

Fig. 4. Hysteresis loops in the CoPt-In_2O_3 nanocomposite film plane and the perpendicular plane

Fig. 4 presents the hysteresis loops measured in the CoPt-In_2O_3 film plane and the perpendicular plane. They have a coercivity of $H_c \sim 150$ Oe, and a saturation magnetization of $M_s \sim 600$ emu/cm^3. The relatively large ratio $M_r/M_s < 0.3$ between the remnant magnetization M_r and saturation magnetization M_s (Fig. 4) shows that the CoPt nanoparticles consist of randomly oriented grains with a cubic magnetocrystalline anisotropy [29].

Conclusion

The main results of our investigations are as follows. The low-coercivity CoPt-In_2O_3 nanocomposite films were obtained by annealing the In/(Co_3O_4 + Pt)/MgO(001) samples in a vacuum at 10^{-6} Torr in the temperature range of 100 − 800 °C with a step size of 100 °C and exposure at each temperature for 40 min. Comprehensive structural and magnetic investigations unambiguously indicate that after annealing the film contains CoPt (A1-CoPt + $CoPt_3$ + Co_3Pt) alloy nanograins by the In_2O_3 layer, with an average size of 5 nm. The synthesized CoPt-In_2O_3 film nanocomposites had a magnetization of about 600 emu/cm^3 and a coercivity of about 150 Oe at room-temperature. The initiation 200 °C and finishing 800 °C temperatures of synthesis and the phase composition of the reaction products were determined. It has been suggested that the formed In_2O_3 phase prevents the transition of the cubic CoPt phase to the tetragonal $L1_0$-CoPt phase and, as a result of the synthesis, low-coercive films were formed. Thus, the solid-state method is promising for synthesizing ferromagnetic nanocomposite thin films consisting of ferromagnetic nanoparticles.

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Магнитные и структурные свойства нанокомпозитных пленок CoPt-In_2O_3

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Аннотация. Исследованы структурные и магнитные свойства нанокомпозитных пленок CoPt-In_2O_3, полученных вакуумным отжигом пленочной системы In/(Co_3O_4 + Pt)/MgO в интервале температур 100 – 800 °C. Синтезированные нанокомпозитные пленки содержали ферромагнитные CoPt-кластеры со средним размером 5 nm, заключенные в матрицу In_2O_3, и имели намагниченность 600 emu/cm^3, коэрцитивную силу 150 Oe при комнатной температуре. Определены температуры начала 200 °C и окончания 800 °C синтеза, а также изменение фазового состава пленки In/(Co_3O_4 + Pt)/MgO при вакуумном отжиге.

Ключевые слова: тонкие пленки, ферромагнитные нанокомпозиты, сплав CoPt, оксид In_2O_3.