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LOW-DIMENSIONAL SYSTEMS AND SURFACE PHYSICS

Self-Propagating High-Temperature Synthesis in Pt/Co/MgO(001) Epitaxial Thin Films

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Abstract—The self-propagating high-temperature synthesis in the two-layer and multilayer Pt/Co(001) thin films has been investigated. It is shown that the initiation of the synthesis occurs at temperatures of 770–820 K. After the synthesis in the two-layer film samples, the PtCo(001) disordered phase exhibits an epitaxial growth at the interface between cobalt and platinum layers. In the multilayer Pt/Co(001) thin films, the self-propagating high-temperature synthesis also brings about the formation of the PtCo(001) disordered phase on the MgO(001) surface. Further annealing at a temperature of 870 K for 4 h results in the transition of the PtCo(001) disordered phase to the ordered phase. Rapid thermal annealing of the Pt/Co(001) multilayer films at a temperature of 1000 K leads to the formation of the $CoPt_3$ phase. The magnetic characteristics change in accord with the structural transformations in Pt/Co film samples. © *2000 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

In recent years, intensive studies of the Pt/Co multilayer films have been caused by their possible use as a medium for high-fidelity magnetooptical recording [1–7]. The Pt/Co multilayers deposited onto glass substrates are characterized by the (111) texture and a considerable perpendicular magnetic anisotropy whose nature remains unclear. In the Pt/Co/MgO(001) epitaxial multilayer films, the easy magnetization axis either can be aligned perpendicular [8] or within the plane of the film [9, 10], or can form an angle with the sample plane [11]. In the course of annealing [8, 12] or ionic bombardment [13], the structural and magnetic properties of the Pt/Co multilayer films exhibit substantial changes. Actually, the Pt/Co/MgO(001) multilayer films due to annealing in the temperature range 475–675°C for 14 h undergo a transformation into the CoPt ordered tetragonal phase with the *c* axis perpendicular to the surface of the sample [8, 12].

However, in analyzing the results of heat treatments or the action of ionic bombardment, it is usual practice to ignore the possibility of initiating the self-propagating high-temperature synthesis between cobalt and platinum layers. Unlike the self-propagating high-temperature synthesis occurring in powders, which is rather well understood [14], this process in thin films has come under the scrutiny of science only in the very recent years [15, 16]. Upon fast heating of the two-layer film samples above the initiation temperature T_0 at a rate of higher than 20 K/s, the self-propagating high-temperature synthesis in thin films proceeds in the form of a surface combustion wave. Since the velocity of the front of self-propagating high-temperature synthesis at temperatures close to the initiation temperature T_0 is equal to $\sim(0.2–0.5) \times 10^{-2}$ m/s, its propagation can be observed visually. The temperature of the front is considerably higher than the temperature of the rest of the film, and, hence, most of the mass transfer and the formation of reaction products take place solely at the front of self-propagating high-temperature synthesis. As a result, upon fast cooling at the rear of the front, the metastable, quasicrystalline, and amorphous phases, apart from the equilibrium compounds, can be formed in the reaction products [15–17].

The purpose of the present work was to investigate the self-propagating high-temperature synthesis and its influence on the structural and magnetic properties of the epitaxial two-layer and multilayer Pt/Co/MgO(001) films.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The two-layer and multilayer Pt/Co film samples were prepared by the ion–plasma sputtering onto glass substrates and onto the freshly cleaved MgO(001) surfaces. The total thickness of cobalt was equal to 30–50 nm, and the total thickness of platinum was 50–70 nm. In the experiments, their ratio was taken to be close to the atomic ratio 1 : 1. The character of the

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propagation of high-temperature synthesis essentially depends on the thermal properties and substrate thickness. In order to decrease the heat transfer into the substrates, their thicknesses were taken to be minimum as far as possible. The glass substrates used in the experiments were 0.18 mm thick, and the thickness of the MgO substrates was varied in the range from 0.35 to 0.40 mm. The Pt/Co two-layer film samples were produced by the sequential evaporation of cobalt and platinum layers onto a substrate in the following way: the cobalt film was first evaporated at a temperature of 550 K, and then, the platinum layer was applied at a temperature of 300 K. The Pt/Co epitaxial multilayers were deposited at a temperature of 550 K onto the MgO(001) substrates and contained from 60 to 90 pairs of the cobalt and platinum layers. The thicknesses of cobalt and platinum layers in each pair fell in the ranges 0.40–0.44 and 0.51–0.55 nm for cobalt and platinum, respectively.

The phase composition of the samples was determined on a DRON-4-07 instrument (K_α-radiation). The X-ray fluorescence analysis was employed to determine the chemical composition and thickness of the studied films. The magnetic properties of samples were examined with the use of vibrating-sample and torsional magnetometers. The biaxial anisotropy constant was determined as $2l_{max}$, where l_{max} is the maximum torque moment per unit volume of the sample. To initiate the self-propagating high-temperature synthesis, the samples prepared were placed on a tungsten heater to produce a uniform temperature field in the sample plane. The heating was performed under a vacuum of $\sim 1 \times 10^{-3}$ Pa at a rate of no less than 20 K/s up to the temperature T_0 of the initiation of self-propagating high-temperature synthesis followed by cooling at a rate of ~10 K/s.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The self-propagating high-temperature synthesis in the Pt/Co two-layer films deposited onto glass substrates was initiated at temperature T_0 = 770–820 K. The front of the propagation of high-temperature synthesis was observed visually (Fig. 1). A visual observation showed that the self-propagating high-temperature synthesis proceeded across the whole width of the film sample.

Figure 1 demonstrates the autowave motion of the front of self-propagating high-temperature synthesis, which is typical of the two-layer film samples [15, 16]. The temperature profile of the front and the mechanism of its autowave propagation were described in [15, 16]. However, in the case of the two-layer and multilayer Pt/Co films deposited onto the MgO(001) substrates, the motion of the front of self-propagating high-temperature synthesis was not visually observed. This can be due to the fact that the heat transfer from the front to the substrate is quite significant even if the thickness of the MgO substrate is equal to ~0.35 mm. As a consequence, the temperature of the front decreases, and the wave of self-propagating high-temperature synthesis covers only the thin boundary layer between platinum and cobalt, which is invisible to the eye. An alternative explanation resides in the fact that, upon reaching the initiation temperature T_0, the self-propagating high-temperature synthesis proceeds throughout the phase boundary rather than in the form of a surface combustion wave. Hence, the cycle of the self-propagating high-temperature synthesis consisted in heating the two-layer and multilayer Pt/Co/MgO(001) film samples at a rate of higher than 20 K/s up to a temperature of 870 K, which exceeded the initiation temperature T_0. Thereafter, the samples were allowed to stand at this temperature for 30 s, followed by cooling at a rate of ~10 K/s. This time is large enough for the self-propagating high-temperature synthesis to extend over the whole sample, including the induction period.

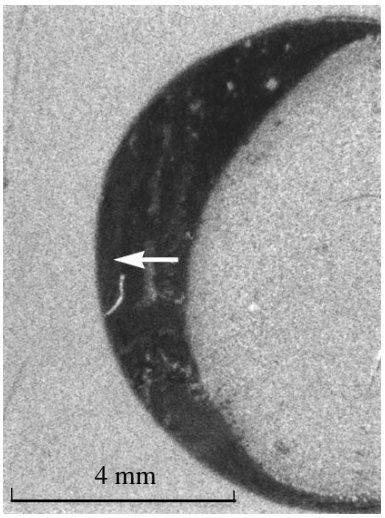

Fig. 1. A micrograph of the self-propagating high-temperature synthesis in the Pt(50 nm)/Co(40 nm) film on a glass substrate 0.18 mm thick. The arrow indicates the direction of the front of self-propagating high-temperature synthesis.

The heat treatment similar to the above cycle of self-propagating high-temperature synthesis is often employed in thin films and is referred to as the rapid thermal annealing [18]. The rapid thermal annealing was also used in studies of the Fe/Pt nanoscale multilayers [19].

The X-ray diffraction patterns of the Pt/Co/MgO(001) two-layer film samples prior to the initiation of the self-propagating high-temperature synthesis indicated that the β-Co film grew up with the (001) orientation on the MgO(001) surface at the substrate temperature T_s = 470 K. The upper platinum layer, which was deposited onto the β-Co(001) film at the temperature T_s = 300 K, grew up with the predominant (001) orientation. However, in this case, the (111) orientation of the platinum phase is also observed, but to a lesser degree (Fig. 2a). According to the magnetic measurements, the

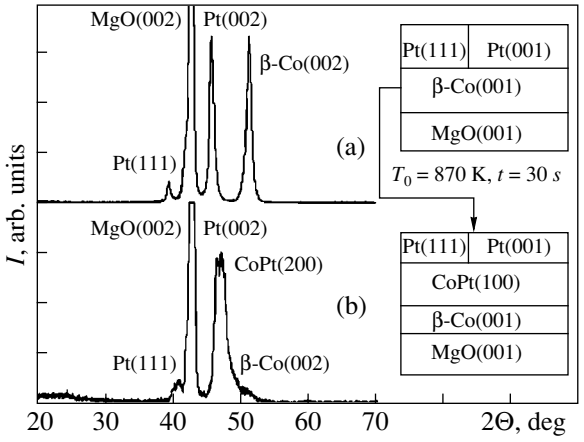

Fig. 2. X-ray diffraction patterns and schematic diagrams of the phase composition and phase orientation in the Pt(50 nm)/Co(40 nm)/MgO(001) two-layer films: (a) initial sample and (b) sample after the cycle of self-propagating high-temperature synthesis.

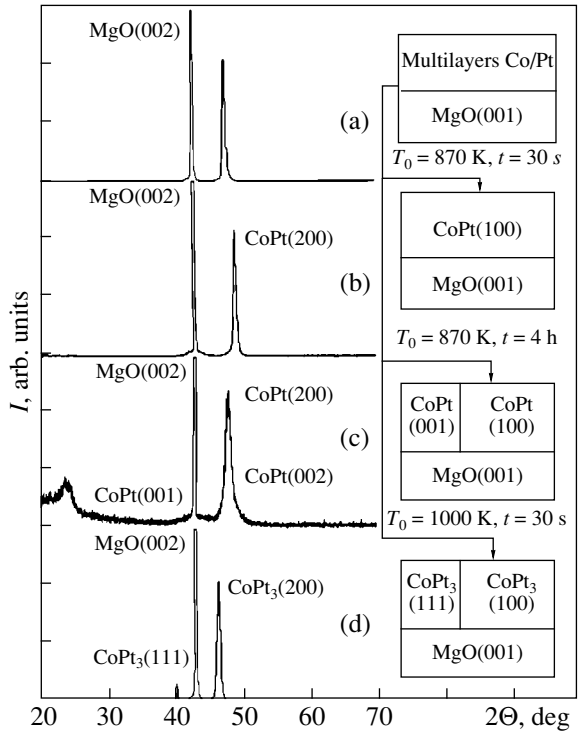

Fig. 3. X-ray diffraction patterns and schematic diagrams of the phase composition and phase orientation in the Pt(5.3 nm)/Co(4.2 nm)/MgO(001) multilayer films: (a) initial sample and samples after (b) the cycle of self-propagating high-temperature synthesis, (c) annealing at a temperature of 870 K for 4 h, and (d) annealing at a temperature of 1000 K for 30 s.

saturation magnetization I_s and the first constant of magnetocrystalline anisotropy K_1 for these samples (per unit volume of the cobalt film) correspond, respectively, to the values of I_s and K_1 for the β-Co phase.

An analysis of the X-ray diffraction patterns and magnetic measurements demonstrate that the β-Co film and the MgO substrate are characterized by the epitaxial relationships (001), Co[100] ∥ (001), MgO[100], which were observed earlier in [20]. The X-ray diffraction patterns of samples after the cycle of self-propagating high-temperature synthesis indicate that, in addition to the residual layers of cobalt and platinum, the reaction products contain a layer of the CoPt disordered phase with a coherent orientation with respect to the (001) plane. As follows from the magnetic measurements, the self-propagating high-temperature synthesis between cobalt and platinum layers proceeds not across the whole width of the film sample, but extends for a depth of no more than 25–30 nm (Fig. 2b). The biaxial anisotropy in the plane of the sample increases by a factor of 1.5–2 after the cycle of self-propagating high-temperature synthesis, whereas the easy magnetization axes do not change their directions.

The discrepancy between the lattice parameters of the β-Co and CoPt phases has a minimum value when the CoPt disordered phase grows in an epitaxial fashion and, in the case of the β-Co matrix phase, follows the orientational relationships (100), CoPt[100] ∥ (100), Co[100]. This implies that the CoPt disordered phase, like the β-Co matrix phase, possesses the negative magnetocrystalline anisotropy. Similar epitaxial relationships are observed upon self-propagating high-temperature synthesis in the Al/Fe/MgO(001) two-layer films [21]. It seems likely that the cooling at high rates makes impossible the formation of the CoPt equilibrium tetragonal ordered phase.

The X-ray diffraction patterns of the Pt/Co/MgO(001) multilayer film samples prior to the initiation of the self-propagating high-temperature synthesis exhibit a peak corresponding to the lattice parameter intermediate between the unit cell parameters of cobalt and platinum (Fig. 3a). The absence of large-angle and small-angle satellite reflections suggests a partial mixing between the cobalt and platinum layers. The magnetic measurements show that the easy axes of the Pt/Co/MgO(001) multilayers coincide with the MgO[111]-type directions rather than lie in the plane of the film. As follows from the curves of torque moments measured in the (100), (010), (001), (110), and MgO($1\bar{1}0$) planes, the magnetocrystalline anisotropy of the Pt/Co/MgO(001) multilayer films is adequately described by the anisotropy constant $K_1 = 1 \times 10^6$ erg/cm^3, which considerably exceeds the shape anisotropy of the sample $2\pi I_S^2$ ($K_1 \gg 2\pi I_S^2$). The measured values of the saturation magnetization of these samples (I_s = 200–220 emu/cm^3) satisfy this inequality. This gives grounds to believe that the multilayers under consideration are not a superposition of cobalt and platinum layers, but represent a weakly modulated phase that consists of mutually penetrating layers of cobalt and platinum.

After the cycle of self-propagating high-temperature synthesis, the diffraction peak shifts and, thus, corresponds to the reflection from the (200) plane of the CoPt disordered phase (Fig. 3b). The magnetic properties of the samples upon self-propagating high-temperature synthesis exhibit radical changes. The plane of the film becomes the easy magnetic plane. The easy axes of magnetization in the plane of the film do not change their directions; however, the biaxial anisotropy in the film plane and the saturation magnetization increase up to the values of $2l_{max} = (2.5–2.0) \times 10^6$ erg/cm^3 and $I_s = 560–580$ emu/cm^3, respectively. From the foregoing, it is evident that the CoPt disordered phase epitaxially grows on the MgO(001) surface in the same manner as in the course of growth in the Pt/Co two-layer films, follows the orientational relationships (100), CoPt[100] ∥ (100), MgO[100], and has the first magnetocrystalline anisotropy constant $K_1 = -(2.5–2.0) \times 10^6$ erg/cm^3.

In the experiments, we also used the thermal annealing of the Pt/Co/MgO(001) multilayer films at a temperature of 870 K for 4 h. After the annealing, the easy magnetization axes are located at an angle of 10–15 deg with the plane of the film, rather than lie within this plane. The biaxial magnetic anisotropy in the plane of the sample retains the directions of easy magnetization axes. However, the magnetic anisotropy and the coercive force along the direction of easy magnetization drastically increase and become equal to $(10–12) \times 10^6$ erg/cm^3 and 10 kOe, respectively. That large values of the magnetic anisotropy and coercive force correspond to the formation of the CoPt tetragonal ordered phase [8, 12]. This is corroborated by the diffraction data. The X-ray diffraction patterns of these samples display the (002) reflections and also the (001) superstructure reflections from crystallites of the CoPt tetragonal ordered phase, which is oriented by the *c* axis perpendicular to the film plane (Fig. 3c). The presence of reflections from the CoPt(200) phase suggests that crystallites of the CoPt tetragonal phase are ordered by the *c* axis along three mutually perpendicular axes of the MgO phase. The magnetocrystalline anisotropy energy E_K of the tetragonal crystal per unit volume of the sample without regard for anisotropy in the basal plane can be written in the following form: $E_K = E_0 + K_1 \sin^2\theta + K_2 \sin^4\theta$, where θ is the angle between the magnetization I_s and the *c* axis. Under the assumption that crystallites of the CoPt ordered phase equiprobably grow with the *c* axes along three mutually perpendicular axes of the MgO phase, the magnetocrystalline anisotropy energy of this film system can be represented as $E_K = E_0 + 1/6K_2(\sin^2 2\psi \sin^4\psi \sin^2 2\phi)$, where ϕ is the angle between the projection of the magnetization I_s onto the film plane and the MgO[100] axis, and ψ is the angle between the magnetization I_s and the normal to the film. The torque moment curve $L = -dE_K/d\phi$ in the plane of the sample ($\psi = \pi/2$) has a maximum that can be determined as $2l_{max} = K_2/3$; the experimental value of this maximum is equal to $(1.0–1.2) \times 10^7$ erg/cm^3. From this, one can obtain the second constant of magnetocrystalline anisotropy $K_2 = (3.0–3.6) \times 10^7$ erg/cm^3 for the PtCo ordered phase. The CoPt ordered phase of the bulk alloy is characterized by the values $K_1 = 5 \times 10^7$ [22] and $K_1 + K_2 = 2 \times 10^7$ erg/cm^3 [23]. The found value of the second magnetocrystalline anisotropy constant $K_2 = (3.6–4.2) \times 10^7$ erg/cm^3 for the PtCo ordered phase on the films is inconsistent in sign with the K_2 value for the bulk samples.

The magnetic measurements of the Pt/Co/MgO(001) multilayer films after the cycle of self-propagating high-temperature synthesis carried out at a temperature of 1000 K demonstrate that no anisotropy is observed in the plane of the sample. In this case, the samples exhibit a low saturation magnetization (~100 emu/cm^3) with the easy magnetic plane coinciding with the plane of the film. The diffraction patterns indicate that crystallites of only the $CoPt_3$ phase with the predominant orientation of the (001) plane parallel to the MgO(001) plane are formed in the samples. There exists also a small amount of the $CoPt_3$ phase with an orientation of the (111) plane parallel to the MgO(001) plane (Fig. 3d). The $CoPt_3$ ordered phase is nonferromagnetic at room temperature, whereas the $CoPt_3$ disordered phase possesses the magnetization equal to 500 emu/cm^3 [24]. Hence, it follows that the $CoPt_3$ phase formed during the self-propagating high-temperature synthesis exhibits a larger degree of ordering. The sequences of the phase formation with an increase in the annealing temperature, which are similar to the sequence Pt/Co ⟶ CoPt ⟶ $CoPt_3$, can be frequently observed in the solid-phase reactions. As mentioned above, the Pt/Co/MgO(001) multilayer films, as well as the CoPt phase formed upon the heat treatment, have the larger negative magnetocrystalline anisotropy constant K_1. Therefore, in the Pt/Co multilayer films with the (111) texture, the easy magnetization axis is perpendicular to the plane of the sample, and the perpendicular magnetic anisotropy constant is primarily determined by the magnetocrystalline anisotropy constant K_1. It is important to keep in mind that the temperature of the initiation of self-propagating high-temperature synthesis $T_0 = 770–820$ K for the Pt/Co film samples coincides with the ordering temperature for the CoPt alloy [25]. This gives grounds to assume that there is a certain interrelation between the chemical mechanisms of the synthesis and ordering. The FePt phase is formed as the result of annealing in the Fe/Pt multilayer films [8, 12, 19, 26]. Hence, it can be expected that the self-propagating high-temperature synthesis should be initiated in the two-layer and multilayer Fe/Pt film samples with the formation of the FePt phase in the reaction products.

Therefore, in the Pt/Co two-layer films deposited onto glass substrates, the self-propagating high-temperature synthesis in the form of a surface combustion wave is initiated between the cobalt and platinum layers at temperatures $T_0 = 770–820$ K and proceeds across the whole width of the film sample provided that

the total thickness of the films does not exceed 100 nm. In the same film samples, but deposited onto the MgO substrates, the self-propagating high-temperature synthesis covers an interphase boundary between cobalt and platinum whose thickness is equal to 20–30 nm. After the cycle of self-propagating high-temperature synthesis at temperatures T_0 = 770–820 K, the reaction products contain a layer of the CoPt disordered phase, which epitaxially grows on the surfaces of cobalt and platinum. Upon annealing at a temperature of 870 K for 4 h, the CoPt disordered phase undergoes a transformation into the ordered phase. It is assumed that crystallites of the CoPt ordered tetragonal phase equiprobably grow with the *c* axes, which coincide with the crystallographic directions of the MgO[100] type. This assumption made it possible to determine the constant $K_2 = (3.0–3.6) \times 10^7$ erg/cm^3 in the expression of the magnetocrystalline anisotropy energy for the CoPt ordered tetragonal phase. The cycle of self-propagating high-temperature synthesis in the Pt/Co/MgO(001) multilayer films at a temperature of 1000 K results in the formation of the $CoPt_3$ phase, which grows with the predominant (100) orientation on the MgO(100) surface.

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