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Synthesis and Magnetic Properties of $[(CoP)_{soft}/NiP/(CoP)_{hard}/NiP]_n$ Films

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Abstract Magnetic interactions in Co–Ni–P multilayers consisting of alternating magnetically soft and magnetically hard layers are experimentally investigated. The variation in the shape of magnetization loops at the conjugation of magnetically soft and magnetically hard layers and the saturation field oscillations with varying number of layer pairs are established. It is demonstrated that insertion of a nonmagnetic spacer significantly affects the magnetization reversal in the structure. It is concluded that in studying the interlayer coupling it is necessary to take into account the biquadratic interaction.

Keywords Magnetic heterostructure · Hysteresis loop · Interlayer coupling · Magnetic spring

1 Introduction

Multilayer magnetic film structures attract attention of researches since, selecting the order of layer deposition, materials of magnetic and nonmagnetic layers, and a number of layers in a structure, it is possible to fabricate materials with unique properties [1]. The interlayer coupling in the described systems is responsible for the formation of the magnetic state and causes some intriguing phenomena. The conjugation of ferromagnetic (FM) and antiferromagnetic (AFM) layers leads, as a rule, to implementation of the exchange bias, and the magnetization process as a whole is related to the behavior

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of the FM layer [2]. Here, we observe the shift of hysteresis loops along the magnetic field direction, the significant growth of the coercivity of the ferromagnet, and anomalies of the rotational hysteresis of the multilayer. At the conjugation of magnetically soft and magnetically hard FM layers, a new, magnetic spring state occurs, when the magnetization process involves certain stages and the hysteresis loop has a specific shape [3]. The first experimental implementation of the exchange-spring principle was reported in [4]. When the external field is applied to such bilayers, spins of the neighboring magnetically soft layers rotate from the effective field direction near the interface separating the magnetically soft and magnetically hard materials to the external field direction. Earlier, these systems were studied in the context of heterophase systems [5–7] and multicomponent permanent magnets [8]. Some features of magnetization switching, including the exchange shift of the partial hysteresis loop, critical fields of the onset of magnetic spiral formation, and reversibility of the initial switching stage, were qualitatively explained. Then, these investigations were extended to the features of magnetization in inhomogeneous layered structures with different thicknesses of the magnetically soft and magnetically hard layers, interlayer coupling, and anisotropy of the layers [9,10]. If the soft phase is unconfined, it can form a noncollinear or twisted magnetization structure to attempt following either the external or demagnetizing field. The layered structures are interesting for spintronics applications, including magnetic sensors based on the magnetoresistive effect. This effect can be enhanced by the creation of multilayer (more than two layers) magnetic structures that behave similar to magnetic springs. We devoted our report to the magnetization processes in multilayer film structures that consist of alternating magnetically soft and magnetically hard layers separated by the nonmagnetic spacer and have different numbers of structural blocks.

2 Experimental

Fabrication technology plays an important role in creation of new structures [11], since, as a rule, it determines their physical properties. Film structures are mainly obtained by sputtering or electro- or chemical deposition techniques. The latter are attractive for prediscovery due to their relative simplicity and high rate. Therefore, we formed the $[(CoP)_{soft}/NiP/(CoP)_{hard}/NiP]_n$ films by chemical deposition. In addition, this technique allows obtaining high-quality interfaces, since the layer formation in the course of the interfacial reaction occurs under the conditions close to equilibrium.

When choosing the cobalt-based magnetic layer material, we were guided by the fact that the conductivity of a substance is determined by the electron density of states (D) at the Fermi level [12]. The polarization of conduction electrons is expressed as [13] $P = [D_{\uparrow}(E_F) - D_{\downarrow}(E_F)]/ [D_{\uparrow}(E_F) + D_{\downarrow}(E_F)]$, where $D_{\downarrow,\uparrow}$ is the density of states at the Fermi level for "spin-up" and "spin-down". Using the calculated electron density of states for cobalt, we obtain the estimates $P \approx 60$ % for the hexagonal (hcp) phase [14] and $P \approx 90$ % for the cubic (bcc) phase [15]. Upon electron tunneling from cobalt through the Al_2O_3 spacer, the degree of spin polarization of tunneling electrons is $P_{tun} \approx 42$ % [16].

The phosphorous content in all the layers was 8 at.%. In the magnetically hard layer, CoP was in the hexagonal polycrystalline state and in the magnetically soft layer, in the amorphous state with nickel content 27.6 % aT. and cobalt content 64.4 % aT. It is well known [17] that in the $Co_{1-x}Ni_xP$ alloys with a nickel content $x > 0.7$, the material transforms to the paramagnetic state and its structure (amorphous or crystalline) is determined by the solution composition, deposition rate, and phosphorous content. In our case, the intermediate NiP layer was amorphous and nonmagnetic [18] with a thickness $t_{\mathrm{NiP}} = 2$ nm. Such a composition of the layers was chosen because of the absence of sharp structural variations at the interface. The layer thicknesses were chosen such as to the interlayer interaction energy be comparable with the Zeeman energy of the ferromagnetic layer and the interlayer interaction effects not be masked by other interactions.

The layer thicknesses were measured by X-ray spectroscopy with a measurement accuracy of ± 0.5 nm. Surface roughness was measured by a Veeco MultiMode NanoScope IIIa SPM system with a resolution of up to 0.2 nm and amounted to ± 1 nm in height in the maximum on a basis length of 20 nm. Magnetic characteristics were measured on an MPMS-XL magnetic property measurement system operating in the temperature range 78–900 K in magnetic fields of ≤ 17 kOe. In the experiment, the magnetic field was in the film plane. The size of the multilayer film was 5×5 mm^2. In the experiment, the magnetic moment of unit area of film (ϕ) was measured.

3 Results and Discussion

Two series of films were investigated: (I)—the first series did not have separation layers and both magnetic layers had a thickness $t = 4$ nm, and (II)—both magnetic layers had a thickness $t = 5$ nm and $t_{\mathrm{NiP}} = 2$ nm.

Previously [19], we investigated structural variations on the surface of polycrystalline CoP films of different thicknesses by atomic force microscopy and found the film mesostructure at small thicknesses to be a set of weakly bound crystallite nuclei with randomly oriented easy magnetization axes. As the film thickness is increased, a homogeneous polycrystalline layer forms. In addition, the correlation between the magnetic and magnetooptical properties of the CoP films and their surface mesostructure was established.

It is shown [20] that $\mathrm{CoNiP_{soft}}$ and $\mathrm{CoP_{hard}}$ are typical ferromagnets (Fig. 1a, b) and the coercivity of the magnetically soft layer decreases by more than an order of magnitude, while the coercivity of the magnetically hard layer halves as the temperature is increased from liquid nitrogen to room. The situation becomes noticeably different when these two layers form a sandwich. It can be seen that the magnetization curve represents the superposition of two loops (Fig. 1c). This is, however, not an algebraic sum of the initial curves, since the inner loop is broadened as compared with the initial magnetically soft curve and the outer loop is noticeably narrowed. The magnetic spring-type structures exhibit a specific hysteresis loop [8]. As the number of layer pairs in such structures increases, the magnetization curve becomes smooth, without steps and waists, and significantly narrows (Fig. 1d). Let us note one more interesting point related to the behavior of the magnetization saturation field Fig. 2.

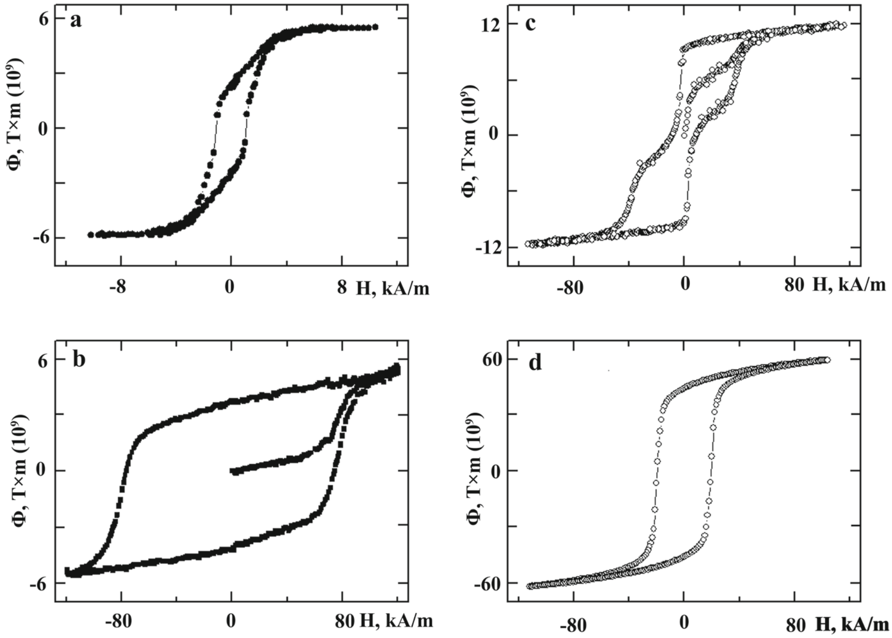


Fig. 1 Field dependence of the magnetic moment (ϕ) of unit area of film for [CoP/CoNiP]$_n$ films. **a** single magnetic soft layer, **b** single magnetic hard layer, **c** two-layer film ($n = 1$), **d** five-layer film ($n = 5$). Temperature $T = 78$ K

Since the magnetization curve contains a long inclined portion (almost straight line, i.e., the paramagnetic tail), the saturation magnetization field was determined from the curve ∂M(H,T)/∂H in increasing field in the range $H > 0$ as the cross point of the horizontal curve and the asymptote of the descending portion in the magnetization curve derivative. The saturation field H_S of the films with even numbers of layer pairs (curves 3 and 5) is higher than that of the films with odd numbers of layer pairs. The experimental results indicate that the interlayer interaction is comparable in the order of magnitude with the intralayer exchange interaction. Otherwise, if the interlayer and intralayer interactions in the multilayer structure will be noticeably different, the resulting magnetization curve will have a complex shape with kinks or steps. In our case, the smooth magnetization curves with a classical shape are indicative of magnetization reversal of the entire film structure.

The dependences in Fig. 1c can be understood if we assume that a magnetically soft layer magnetizes a magnetically hard one due to interlayer exchange interaction, which reduces the saturation field. The behavior of the curves in Fig. 2 suggests that in the multilayer structures with an odd number of layer pairs, there is an additional uncompensated contribution determined by the mechanism responsible for the canted structure. Assuming that this contribution is related to the grain anisotropy, it must be compensated completely, regardless of the number of layers. Another mechanism, related to the presence of either negative exchange interaction between magnetically hard layers via magnetically soft ones or to negative biquadratic exchange between magnetically soft and hard layers, is also possible.

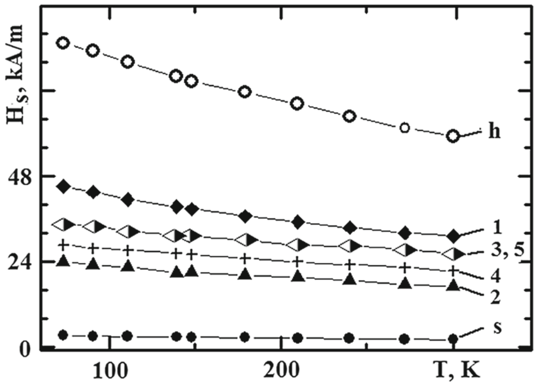


Fig. 2 Temperature dependences of saturation field of [CoP/CoNiP]$_n$ films. s, h—magnetic soft layer, single magnetic hard layer, 1, 2, 3, 4, 5—n = 1, 5, 10, 15, 20, respectively

Insertion of the nonmagnetic NiP layer strongly changes the situation. At small values of n, when the interrelation of the magnetically soft and magnetically hard layers is weakened by the nonmagnetic layer, the coercivity of these films is lower than that of the films without nonmagnetic spacer (compare curves in Figs. 1c and 3a). As one can see in Fig. 3 that field H_{ir}, which determines the onset of irreversible processes during magnetizing [7], decreases with increasing number of blocks. In addition, one can see that in the irreversible magnetization regime, field H_{ir} decreases with increasing number of blocks n. For the films with $n > 10$, the hysteresis width decreases with increasing number of structural blocks (see Fig. 3b, c), however, the stepwise shape of the magnetization curve remains. (see Fig. 3b, c). One can see that the magnetic spring effect becomes more pronounced as the number of structural blocks increases.

Since the magnetic spring effect in multilayer structures has not been theoretically investigated, we will make the estimations using the results obtained for a bilayer film with strong interlayer coupling and sharp boundary between neighboring magnetic layers. This analysis is allowed in the mean-field approximation, when the limit transition to the sublattice consideration is justified within a continuous medium model (magnetically soft and magnetically hard sublattices).

In this approach, the coercivity of a structure is [21]

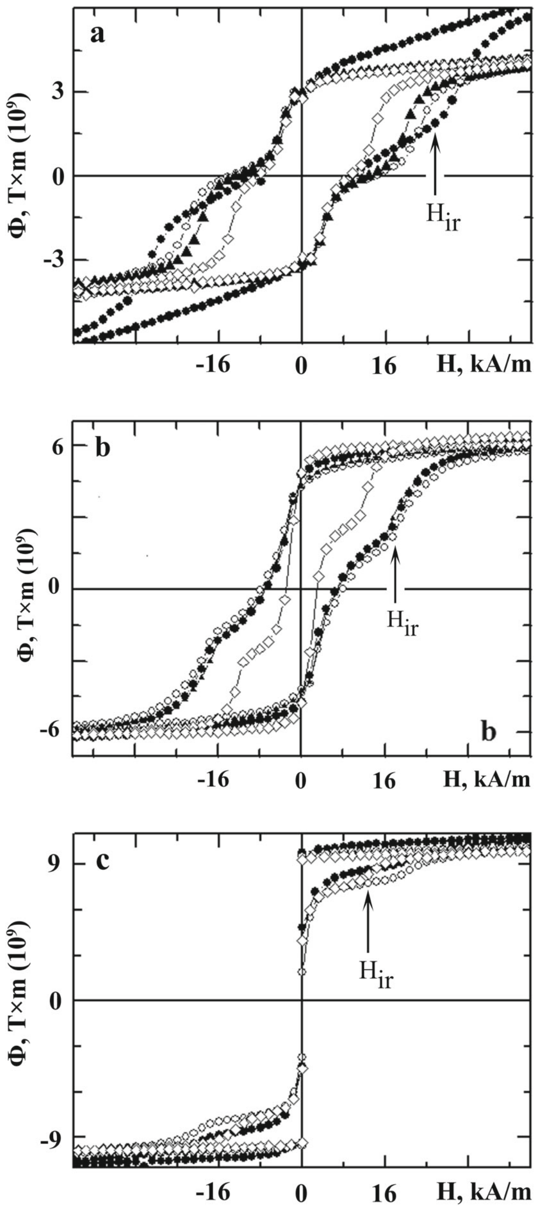
$$H_{\mathrm{C}} = [2 \times K_{\mathrm{hard}}/M_{\mathrm{hard}}] \times [1 - \varepsilon_{\mathrm{K}} \times \varepsilon_{\mathrm{A}}] / \left[1 + (\varepsilon_{\mathrm{M}} \times \varepsilon_{\mathrm{A}})^{1/2}\right]^2, \tag{1}$$

where, $\varepsilon_{\mathrm{K}} = K_{\mathrm{soft}}/K_{\mathrm{hard}}$, $\varepsilon_{\mathrm{M}} = M_{\mathrm{soft}}/M_{\mathrm{hard}}$, and $\varepsilon_{\mathrm{A}} = A_{\mathrm{soft}}/A_{\mathrm{hard}}$. Here, K_{hard} and K_{soft} are the anisotropy constants, M_{soft} and M_{hard} are the magnetizations, and A_{soft} and A_{hard} are the intralayer exchanges for the magnetically soft and magnetically hard layers, respectively. If the magnetizations and intralayer exchanges of the magnetically soft and magnetically hard layers are identical, the expression for the coercivity is simplified:

$$H_{\mathrm{C}} = (2 \times K_{\mathrm{hard}} - 2 \times K_{\mathrm{soft}})/(4 \times M_{\mathrm{soft}}). \tag{2}$$

It can be seen that the H_{C} value for the magnetic spring is several times lower than the coercivity $H_{\mathrm{C}} = 2 \times K/M$ of a single-domain particle in the Stoner–Wohlfarth

Fig. 3 Field dependence of the magnetic moment (ϕ) of unit area of film for $[(CoP)_{soft}/NiP/(CoP)_{hard}/NiP]_n$. films. **a**, **b**, **c**—$n = 1, 20, 40$, respectively. *Filled circle*—$T = 4.5$ K, *open circle*—$T = 50$ K, *filled triangle*—$T = 100$ K, *open diamond*—$T = 250$ K



theory, which was confirmed experimentally (compare Figs. 1b, c and 3a). There is the maximum in the low-temperature portion of the $H_C(T)$ dependence (Fig. 4); however, the obtained experimental data cannot be explained only by the competition of anisotropies in (2). In addition, in the range $T < 200$ K one can observe oscillations of the H_C value in dependence on the number of blocks (n) in the multilayer structure. It is noteworthy that, as the n value is increased, H_C decreases together with the value

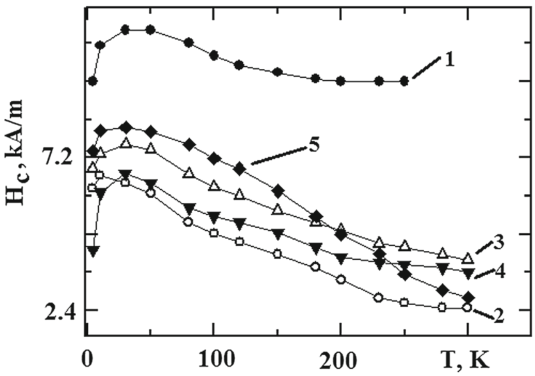


Fig. 4 Temperature dependences of coercivity (H_C) for $[(CoP)_{soft}/NiP/(CoP)_{hard}/NiP]_n$. films. 1, 2, 3, 4, 5—$n$ = 1, 5, 10, 15, 20, respectively

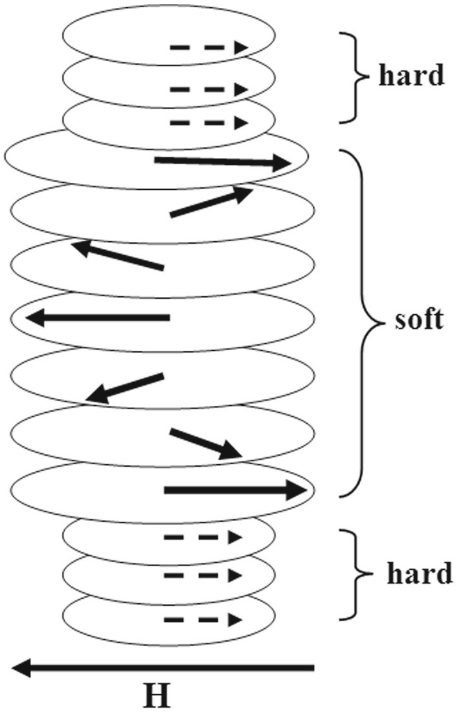


Fig. 5 Sketch of an exchange-spring trilayer

of the high-field step in the $M(H)$ dependence, which can be interpreted as a decrease in the amount of the high-coercivity phase in the structure. Meanwhile, the control thickness measurements at different deposition stages showed that the thicknesses of both the magnetically soft and magnetically hard layers remain invariable.

In contrast to the bilayer structure, in which the magnetically soft layer is pinned to the magnetically hard one and the magnetization starts rotating on a free surface of the magnetically soft layer [22], in our case the magnetically soft layer is located between the magnetically hard layers and its central part is the most sensitive to the magnetic field (Fig. 5). However, a relative compliance of the magnetically soft layer to the magnetic field can be caused by the negative biquadratic interaction at the interface between different materials. In this case, at the interface the unfolded state of magnetization M_{soft} is already implemented, which entails the magnetization of the magnetically hard layer, so the latter is magnetized faster. Then, only the central part of this layer remains really magnetically hard. As far as we know, the biquadratic exchange between two FM layers, magnetically soft and magnetically hard, was reported for the first time in [23]. In addition, the biquadratic interaction in the SmCo–Fe system was found to be magnetic-field-sensitive.

4 Conclusions

It was experimentally demonstrated that an increase in the number of blocks in the structure consisting of magnetically soft and magnetically hard ferromagnetic layers enhances the effect of the magnetically soft layer on magnetization of the film structure, which manifests itself as a decrease in the volume of a magnetically hard material. Insertion of a nonmagnetic spacer causes extraordinary magnetization and coercivity oscillations. The nonmagnetic spacer affects the coupling between ferromagnetic layers. In addition, we may conclude that the biquadratic exchange plays an important role in the formation of magnetic structure in a multilayer film. The authors of studies [24,25] attempted to describe theoretically the behavior of a multilayer structure; however, the consideration was limited to particular cases and there still has been a lack of the general view of the magnetic behavior of such systems.

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