Influence of interface anisotropy on ferromagnetic resonance in CoP/(NiP)am/CoP films

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Abstract
The paper presents the results of ferromagnetic resonance studies of three-layer magnetic films, where the magnetic layers are amorphous magnetically soft CoP layers, and the intermediate non-magnetic spacer is amorphous NiP layer. We found that, regardless of the nonmagnetic layer thickness, the interlayer interaction is ferromagnetic. Perpendicular anisotropy forms at the interface between the CoP and NiP layers. It is reasonable to suppose that the interlayer interaction is long-range, what is not typical for systems with metallic non-magnetic spacers.

1. Introduction
Thin magnetic films containing cobalt attract the researchers’ attention in regards to their possible practical applications [1]. One of the important features of Co-containing materials is a high degree of electron polarization at the Fermi level [2]. In particular, amorphous films of the Co-Ni-P system have high magnetization, low coercive force, and low losses at ultrahigh frequencies [3]. Soft magnetic CoP films (in amorphous modification) have found application as materials for thermomagnetic magneto-optical memory [4] and can be used in microwave devices [5], while hard magnetic CoP films (in hexagonal modification) are considered as promising materials for micro / nano electromechanical systems (MEMS / NEMS) [6]. On the other hand, with using the chemical deposition method for the Co-P system by changing the technological conditions, it is relatively easy to make both magnetically soft and magnetically hard materials. The creation of multilayer structures by combining soft magnetic and hard magnetic layers opens up possibilities for discovering new effects, notably the exchange spring effect [7]. Materials with such behavior have a strong potential for magnetic recording [8] and signal processing applications [9]. Based on the Co-Ni-P system, films [(CoP)soft/(NiP)am/CoP]n, n = 10, ‘am’ is amorphous) were synthesized with behavior similar to exchange springs, where the transformation of the ferromagnetic resonance spectra was found to be dependent on the number of blocks (n) [10]. In this structure, a non-collinear magnetic state arises, where the presumably hard magnetic subsystem splits into two. This circumstance implies a long-range interaction existence, and not only between the nearest neighboring magnetic layers. Also, oscillations in the transport properties of (Ni/Co)n superlattices were observed where nickel and cobalt are in the fcc phase [11].

Thus, in order to exclude effects which can shade the essential moments responsible for the magnetic structure formation of a multilayer film, we studied the features of ferromagnetic resonance in a structure where the magnetic layers of amorphous cobalt are practically isotropic and their thickness fixed, but the thickness of the nonmagnetic layer is variable.

2. Method
Our films were made using electroless chemical deposition method. The deposition of an amorphous CoP magnetic film can be produced in a uniform constant magnetic field of 3 kOe from a solution of cobalt sulfate,
sodium hypophosphite, sodium citrate and ammonia at a temperature of 370 K and pH = 9.5. The deposition of a non-magnetic Ni-P layer can be made from a solution of nickel sulfate, sodium hypophosphite, sodium citrate, ammonium chloride and ammonia at a temperature of 372 K and pH = 7.5. The production technology explained in more detail in [12]. As mentioned above, all layers are in an amorphous state. First, the ferromagnetic layers of amorphous CoP have extremely low magnetic anisotropy (coercive force $H_C \approx 5 - 100$ Oe), which is important when studying interactions in multilayer structures. Second, layers of amorphous NiP are nonmagnetic [13]. The phosphorus content in all layers was about 8 at. %. When the layers being deposited, the synthesis conditions were close to equilibrium. The series of films all was deposited in one cycle, i.e. four substrates were dipped into a solution for the deposition of the CoP layer, then into the solution for the deposition of the NiP layer (the thickness of the resulting NiP layer on substrates with deposited CoP is obviously related to the different immersion times of the substrates in the solution), and at last the substrates were dipped into the solution for CoP deposition.

To get information on the structure of the CoP, NiP layers and the quality of the CoP/NiP interface, cross-section of the samples were made. Cross-section specimens for TEM were prepared by standard technique including cutting, gluing, grinding and polishing the samples to a thickness of 10–15 μm and finally Ar$^+$ ion milling was used to make the specimens electron transparent.

Figure 1(a) shows a bright-field electron microscope image of a cross-section of a CoP/NiP/CoP film (with thickness of NiP layer $t_{NiP} \approx 10$ nm), obtained with a JEOL JEM-2100 transmission electron microscope (TEM). The image shown in figure 1(a) is typical for all studied samples, with the exception of changes in the thickness of the NiP layer. One can see that the layers are not mixed and the interfaces between the layers are not blurred. The thickness of the CoP layers was $t_{CoP} \approx 10$ nm, and the thicknesses of the NiP layer were $t_{NiP} = 0, 1, 4, 12$ nm. Figure 1(b) shows the electron diffraction pattern obtained by the microdiffraction method (selected area electron diffraction (SAED) pattern) from the CoP-NiP layers. SAED pattern is a halo typical for amorphous materials.

Ferromagnetic resonance spectra were measured on a Bruker E580 CW EPR spectrometer operating at a frequency 9.49 GHz. The spectra were processed by fitting the experimental curve of the derivative of the absorption line into the components by derivatives of the Lorentz-type curves.

### 3. Results and discussion

The magnetization measured on a magnetometer for a reference film with $t_{NiP} = 0$ showed a weak, not clear-cut in-plane anisotropy which is also confirmed by in-plane angular-dependent FMR-measurements of all films (figure 2(a)). For field dependences of magnetization, the coercive force varies in the range $H_C \approx 3 - 6$ Oe. A single line is observed in the ferromagnetic resonance spectrum, both in the case when the magnetic field lies in the filmplane and in the case of perpendicular geometry (figure 3). For a nominally pure amorphous NiP film, no resonant microwave absorption signal is observed.
Figure 3 shows the resonance curves at $T = 300$ K for films with $t_{\text{NiP}} = 0$ and $t_{\text{NiP}} = 4$ nm in the case of parallel and perpendicular geometry. For all films with a nonmagnetic interlayer, a single line is observed in case of parallel geometry and the line is shifted relative to the reference film into the region of high fields. Earlier [10], it has also been found that in a two-layer film (CoP)$_{\text{soft}}$/NiP there is a shift in the resonance field magnitude relative to the film (CoP)$_{\text{soft}}$.

In view of the absence of anisotropies, except for the shape anisotropy, the analysis of the temperature dependences of the resonance field $H_r$ for the reference film in figure 4 (curves 1 and 2) was carried out according to standard formulas [14].

$$ \frac{(\omega/\gamma)^2}{\gamma (\omega/\gamma)} = H_{1r} \cdot (H_1 + H_M) $$  \hspace{1cm} (1a)

$$ (\omega/\gamma) = H_{2r} - H_M $$  \hspace{1cm} (1b)

Here $H_1$ and $H_2$ are resonance fields for parallel and perpendicular geometries, respectively, $H_M = 4\pi M$, where $M$ is the magnetization of the CoP layer.

Both experimental sequences of measured points of the resonance field from temperature in figure 4 fit well with the calculated temperature dependences of the resonance field (equations 1(a) and 1(b)) provided that magnetization of the ferromagnetic layer changes according to the Bloch law $T^{3/2}$, namely,

$$ M(T) = M_0 \cdot (1 - \alpha \cdot (T - T_C)^{3/2}) $$  \hspace{1cm} (2)

with fitted parameters $M_0 = 1084.0 \pm 0.6$ emu cm$^{-3}$, $-0.137 \pm 0.020$, $T_C = 853 \pm 5$ K, and $\gamma_{\text{Co}} = (3.020 \pm 0.005) \cdot 10^4$ s$^{-1}$ · G$^{-1}$. The magnetization $M$ at temperature 300 K corresponds to the value for a film with a cobalt thickness $t_{\text{Co}} = 10$ nm [15], and the gyromagnetic ratio $\gamma_{\text{Co}}$ is practically equal to the value obtained for cobalt in the ferrimagnetic structure (Gd/Co)$_n$ [16]. These values will be further used for the analysis of three-layer CoP/NiP$_{\text{am}}$/CoP structures.

Figure 5(a) shows the temperature dependences of the resonance field for all the films studied. The behavior of the resonance field $H_r$ on temperature $T$ looks similar for all samples, i.e. $H_r$ increases with the increasing of $T$. Such dependence cannot be explained only by a simple decrease in the magnetization of the film with
temperature. In addition, figure 5 allows tracing $H_r$ behavior at each measured temperature point. One can see that with increasing of the interlayer thickness the $H_r$ value also increases, but not exceed the maximum value corresponded to the film with $t_{NiP} = 4$ nm. Such a situation is possible if we consider the entire three-layer film as a single structure with ferromagnetic order and the introduction of a non-magnetic layer leads to the appearance of magnetic anisotropy (figure 5(b)). The presence of exactly a single line of resonant absorption indicates a strong ferromagnetic interlayer interaction, otherwise the in-plane angular-dependent FMR-measurements would show splitting of the resonance FMR-signal onto two signals at some angles which we do not observe as could be seen from figure 2. An analysis of the resonant behavior of three-layer films with a nonmagnetic interlayer was performed in [17]. The energy of the system per unit area of the film can be derived from [17] provided that coupling is ferromagnetic, the thickness of the film is very thin, so the shape anisotropy and surface anisotropy dominates the volume anisotropy.

$$E = -t_{3M} \cdot \{HM_A \cos (\alpha_{out} - \theta_A) + HM_B \cos (\alpha_{out}-\theta_B)\}$$

$$+ 2\pi t_{3M} \cdot \{M_A^2 \sin^2 (\theta_A) + M_B^2 \sin^2 (\theta_B)\}$$

$$+ 2K_S [\sin^2 (\theta_A) + \sin^2 (\theta_B)] - KM_A M_B \cos (\theta_A-\theta_B)$$

(3)

here A and B are magnetic layers designations, $t_{3M} = t_A = t_B$–thicknesses of magnetic layers, $\alpha_{out}$ is the angle between the external magnetic field $H$ and the z-axis, which is perpendicular to the filmplane, while $x$-axis and $y$-axis are in the filmplane; $\theta_A (\theta_B)$ is the angle between magnetization $M_A (M_B)$ and z-axis, $K_S$ is surface anisotropy constant, $K$ is the exchange interlayer constant. First term is the Zeeman energy of the layers, the second term is the shape anisotropy energy, the third term is the interface magnetic anisotropy, and the fourth is the interlayer coupling energy.

Figure 4. Temperature dependences of the resonance field of the reference film: 1 (curve with solid dots)–external field is in the filmplane, 2 (curve with empty dots)–external field is perpendicular to the filmplane, solid and empty dots itself represent the experimental data, curves are fitted functions.

Figure 5. Temperature dependences of CoP/NiPam/CoP films: (part a) resonant field, (part b) interface anisotropy field. Curves 1, 2, 3, 4 correspond to interlayer thicknesses $t_{NiP} = 1, 4, 12, 0$ nm respectively.
In the case of two identical ferromagnetic layers, provided that the interlayer interaction is ferromagnetic and its value is much higher than the Zeeman energy of each layer, we can get an expression identical to the one for a ferromagnetic film with magnetic anisotropy.

\[
\frac{(\omega/\gamma)^2}{H_A} = H_A \cdot (H_A + H_A + H_A)
\]

Here \(H_A = 2K_S/(\mu_M \cdot M)\) is the magnetic anisotropy field, and \(M = M_A = M_B\).

Processing the curves in figure 5(a) with using (4) gives the results shown in figure 5(b). One can see that the introduction of an amorphous NiP interlayer leads to the appearance of perpendicular anisotropy (e.g. for a film with \(t_{\text{NiP}} = 12\) nm at \(T = 300\) K, we have \(K_S \approx 10\) erg/cm\(^2\)). A slight increase of anisotropy with increasing temperature is somewhat unusual. Such behavior is possible in film structures [18]. The effect is due to the competition between contributions from the anisotropic exchange of collective electrons and single-ion anisotropy. For example, for the Co\(_m\)/Cu film structure (\(m\) is the number of layers), the magnitude of anisotropy, the change in the sign of the interface anisotropy, and the character of the temperature behavior depend on the thickness of the interface [19].

Some works [20, 21] reported on the presence of perpendicular anisotropy in two-layer films and multilayer structures based on metallic ferromagnets (cobalt and nickel). In those structures, the magnitude of the anisotropy essentially depends on the technological conditions for making the films and on the symmetry of the mating planes. The typical value of the anisotropy energy for the cobalt-nickel interface is \(K_S \approx 2–3\) erg/cm\(^2\) [20] and the anisotropy is perpendicular.

The fact that the resonance line does not split for a film with a large thickness of the nonmagnetic interlayer \(t_{\text{NiP}} = 12\) nm indicates a strong coupling between the magnetic layers. For such interlayer thicknesses this behavior is as a rule not typical. Nevertheless, a direct correlation was found [22] between the magnitude of the anisotropy of the soft-magnetic layer and the exchange coupling between the layers in the structures of a soft-magnetic ferromagnet–hard-magnetic ferromagnet type. This suggests the implementation of a mechanism, in which the appearance of interface anisotropy amplifies the interlayer exchange. As a result, a noncollinear structure can be formed in multilayer structures.

4. Conclusion

The interlayer interaction in the studied films appeared ferromagnetic irrespective of nonmagnetic spacer thickness. Perpendicular anisotropy rises at the interface between magnetic layer and nonmagnetic spacer. A long-range interaction can be realized in multilayer structures, which, along with the induced magnetic anisotropy, can lead to competition of interactions and the appearance of a noncollinear structure.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest

The authors declare that they have no conflicts of interest.

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References

[1] Hirohita A, Yamada K, Nakatani Y, Prejbeani I-L, Dieny B, Pirro P and Hillebrands B 2020 J. Magn. Magn. Mater. 509 166711
[2] Stöhr J and Siegmann H C 2006 Magnetism. From Fundamentals to Nanoscale Dynamics vol 12 (Berlin: Springer) p 524
[3] Belyaev B A, Izotov A V, Kiparisov S Y and Skomorokhov G V 2008 Physics of the Solid State 50 676–83
[4] Treves D, Wolf I W and Ballard N 1969 J. Appl. Phys. 40 976
[5] Podorozhnyak S A, Volochaev M N, Ryzhentsov A V, Chzhant A V, Patrusheva T N and Patrin G S 2016 Elektronika i mikroelektronika SVCh 2 102
[6] Myung N V, Park D-Y, Yoo B-Y and Sumodjo P T A 2003 J. Magn. Magn. Mater. 265 189
[7] Bader S D 2006 Rev. Mod. Phys. 78 1–15
[8] Suess D 2007 J. Magn. Magn. Mater. 308 183–7
[9] Astalos R J and Camley R E 1998 Phys. Rev. B. 58 8646
[10] Patrin G S, Shiyan Ya G, Patrin K G and Furdyk V P 2018 JETP Letters 107 544
[11] Gallego J M, Lederman D, Kim S and Schuller I K 1995 Phys. Rev. Lett. 74 4515
[12] Chzhant A V, Patrin G S and Burkova L V 2012 Method of Producing Amorphous Magnetic Co-P Films RU2501888C1 (https://patents.google.com/patent/RU2501888C1/en)
[13] Colaruotolo J and Tromontana D 1990 Engineering applications of electroweak nickel Electroless Plating: Fundamentals and Applications vol 8 ed G O Mallory and J B Hajdu (Orlando: Fla.: AESF Society) p 208
[14] Baberschke K 2007 Investigation of ultrathin ferromagnetic films by magnetic resonance Handbook of Magnetism and Advanced Magnetic Materials vol 3 ed H Kronmuller and S Parkin (New York: Wiley) p 1617
[15] Chzhant A V, Patrin G S, Kiparisov S Y, Seredkin V A, Burkova L V and Velikanov D A 2011 J. Magn. Magn. Mater. 323 2493
[16] Patrin G S, Vaskovskii V O, Svalov AV, Eremin E V, Panova M A and Vasilev V N 2006 Journal of Experimental and Theoretical Physics 102 131
[17] Layadi A and Artman J O 1990 J. Magn. Magn. Mater. 92 143
[18] Johnson M T, Bloemen P J, den Broeder F J A and de Vries J J 1996 Rep. Prog. Phys. 59 1409
[19] Skomski R 2003 J. Phys.: Condens. Matter. 15 R841
[20] Daalderop G H O, Kelly P J and den Broeder F J A 1992 Phys. Rev. Lett. 68 6882
[21] den Broeder F J A, Janssen E, Mud A and Kerkhof J M 1993 J. Magn. Magn. Mater. 126 563
[22] Guo Z J, Jiang J S, Pearson J E, Bader S D and Liu J P 2002 Appl. Phys. Lett. 81 2029