Multi-Step Magnetization Process of Gd-Co/Co/Cu/Co Thermo-Sensitive Spin Valves

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Abstract: Magnetic and magnetoresistive properties of the Gd-Co/Co/Cu/Co magnetic type multilayered sensitive spin valve were studied as a function of temperature. It is shown that the appearance of a non-collinear magnetic structure significantly affects the shape of the magnetoresistive hysteresis loop. The characteristic values of the critical field related to the appearance of non-collinear structure depend on the temperature of the spin valve. The obtained results can serve as a basis for the improvements of functional properties and expanding the application areas of magnetic multilayered sensitive elements of the spin valve type; for example, for precise determination of the position of the object.

Keywords: spin valves; ferrimagnets; giant magnetoresistance; magnetic multilayers; interlayer coupling; non-collinear magnetic structure

1. Introduction

The change in electric resistance of a ferromagnetic conductor under application of a magnetic field is denominated as magnetoresistance [1]. The discovery of giant magnetoresistance (GMR) in heterostructures [2] and spin valves [3] insured a huge step forward in the modern electronics. Spin valve devices represent a particular class of systems exhibiting GMR at low fields. They can be successfully used as sensitive magnetic field detectors of different types [4,5]. The need for miniaturization of electronics devices, increasing the density of recording information, creation of non-volatile magnetic random-access memories and magnetic biochips stimulates the search for new magnetic materials, the optimal architecture of devices, and the expansion of their functionality [6,7].

Among the various types of the spin valves, rare earth-transition metal alloy-based spin valves are well known [8–12]. Recently, the concept of a thermosensitive spin valve was proposed, and the possibility of its realization was shown [13–15]. In particular, the thermal sensitivity of the Gd-Co/Co/Cu/Co spin valve multilayerd element appears due to the pronounced temperature dependence of the coercive force of the two-layered exchange coupled Gd-Co/Co thin film. Such an artificially created ferrimagnetic material serves as one of the working layers of the magnetic spin valve [13]. The magnetoresistive hysteresis loop of the proposed spin valve sensitive element has the shape which is characteristic for spin valves operating on the basis of the effect of giant magnetoresistance [6]. However, taking into account the ferrimagnetic type of the Gd-Co/Co system, we can expect the appearance of a non-collinear magnetic structure in such a sensitive element in the range of the relatively large fields [16,17]. As a result, the resistance of the spin valve can change...
monotonically and gradually with the change of the external magnetic field. Such a behavior allows not only register the presence/absence of an object, using developed spin valve sensitive element but also to determine its position in a precise way.

In this work, we have designed and fabricated thermosensitive spin valve Gd-Co(35 nm)/Co(7 nm)/Cu(4 nm)/Co(7 nm) magnetic multilayered sensitive elements and studied their magnetic and magnetoresistive properties.

2. Materials and Methods

Magnetic multilayered sensitive elements of spin valve type were prepared by dc-magnetron sputtering. Multilayered structures were deposited at room temperature onto Corning glass substrates in a magnetic field of 250 Oe applied in parallel to the substrate surface direction. Magnetic field was created by specially designed system of permanent magnets aiming to create uniaxial induced magnetic anisotropy in the magnetic layers during the thin film element deposition. Multilayered structures containing Gd–Co, Co, and Cu films were formed by consecutive sputtering of respective targets. In order to prepare Gd$_{23}$Co$_{77}$ layers, a mosaic target that consists of Co disk with small symmetrically arranged Gd tablets located on it was used. The background pressure was $3 \times 10^{-7}$ mbar. An argon gas flow with a pressure of $2 \times 10^{-3}$ mbar was used during the sputtering process.

At the preliminary stage of the selection of the deposition parameters of Gd-Co films, their composition was determined by energy-dispersive X-ray spectroscopy (EDX) using a scanning electron microscope. The microstructure of the films was studied by X-ray diffraction (XRD) using a PHILIPS XPERT PRO automatic diffractometer with CuKα radiation. Magnetic properties of the samples were studied using a vibrating sample magnetometer (VSM). The magnetoresistance (MR) was measured in a Cryogenics Ltd. System using a standard four-probe technique for the samples in the shape of elongated strips ($10 \text{ mm} \times 2 \text{ mm}$ in size), for a direct measuring current of 10 μA. Easy magnetization axis (EMA) of the multilayered structure was parallel to the long side of the stripe. External magnetic field during MR measurements was applied along the EMA.

3. Results

Figure 1 shows the XRD patterns for Gd-Co(35 nm)/Co(7 nm)/Cu(4 nm)/Co(7 nm) sample. An intensive maximum at $2\theta \approx 44^\circ$ position is the consequence of preferential crystal growth and the corresponding orientation of the (002) planes of hcp Co. The average crystallite size for Co layers calculated from the broadening of this X-ray peak using the Scherrer formula was found to be equal to the thickness of Co layers (~7 nm). In comparison to this intense peak, the Cu (111) peak at $2\theta \approx 43^\circ$ was barely visible. This indicates that Cu layer with thickness of 4 nm has poor crystallinity. Finally, the Gd-Co layer was X-ray amorphous as no well-defined additional peaks were observed.

![Figure 1. X-ray diffraction spectrum for Gd-Co(35 nm)/Co(7 nm)/Cu(4 nm)/Co(7 nm) film.](image-url)
The deposition of the investigated films in the presence of a constant magnetic field led to the formation of a pronounced magnetic anisotropy in the plane of the samples, the easy magnetization axis (EMA) coincides with the direction of this field. Such a conclusion can be made as a result of the analysis of magnetic hysteresis loops, measured with a magnetometer along and perpendicular to the EMA (not shown here).

The temperature of the magnetic compensation of the Gd$_{23}$Co$_{77}$ ferrimagnetic layer ($T_{\text{comp}} = 433$ K) agrees well with the value that could be expected based on the composition of the layer and the known dependence of $T_{\text{comp}}$ on the composition of amorphous Gd–Co films [18]. The fact that the compensation temperature is above room temperature means that in the resulting magnetic moment of the Gd$_{23}$Co$_{77}$ ferrimagnetic layer in the entire temperature range, the magnetic moment of the gadolinium sub-lattice prevails. The magnetization vector corresponding to Gd aligns in the direction of the external magnetic field.

A Gd-Co(35 nm)/Co(7 nm) bilayer is a layered artificial ferrimagnet. It has a magnetization compensation temperature $T_{\text{comp}} = 180$ K, at which the moments of the Gd sub-lattice and Co total sub-network cancel each other and the bilayer has no net magnetization [13]. Let us denote the compensation temperature of the Gd-Co(35 nm)/Co(7 nm) bilayer as $T^*$. Below $T^*$, the magnetic moment of the Gd sublattice dominates over that of the Co sub-network (moment of the Co sublattice of Gd-Co layer and moment of Co layer). Above $T^*$, the net Co moment is larger than the Gd moment. The direction of the net Co moment is thus in the same direction as the total moment of the composite layer.

Measurements of magnetoresistive hysteresis loops in the range of the magnetic field of $\pm 6$ kOe showed that the shape of the MR loops varies greatly with the variation of the temperature. Such a behavior can be traced relying on the analysis of three hysteresis loops shown in Figure 2 as typical examples. In the small fields ($H < 700$ Oe), the Gd–Co(35 nm)/Co(7 nm)/Cu(4 nm)/Co(7 nm) multilayer structure hysteresis loop has the form characteristic of spin valves operating on effect of giant magnetoresistance (Figure 2a,c,e). The change of sign of giant magnetoresistive effect and the shape of MR loops is due to the change in the type of the prevailing magnetic sub-system in the two-layered structure Gd–Co/Co. At temperatures above $T^*$, the magnetizations in the Co layers separated by a Cu layer are aligned parallel to each other in a relatively small positive field (Figure 2g(1)). At the same time, the resistance of the spin valve is the lowest. Reversal of the free Co layer when a small negative field is applied leads to an increase in the resistance of the spin valve element (Figure 2g(2) and Figure 2a,c). Conversely, in the temperature range below $T^*$, the magnetizations in the Co layers separated by a Cu layer are arranged antiparallel to each other in a relatively small positive field (Figure 2h(1)). Therefore, the reversal of the free Co layer when a small negative field is applied leads to a decrease in the spin valve element resistance (Figure 2h(2) and Figure 2e).

MR loops indicate that in the field range ($H > 700$ Oe), an additional change in the resistance of the spin valve element occurs (Figure 2,b,d,f). Moreover, the interval of fields in which this change appears, and the value of the fields of the interval are strongly dependent on the sample temperature. Comparison of MR loops and VSM loops (Figures 2 and 3) leads to the conclusion that the change in resistance of the multilayered structure is associated with the appearance of a non-collinear magnetic phase in Gd-Co(35 nm)/Co(7 nm) bilayer. The non-collinear phase arises at a certain critical field $H_{\text{cr}}$ which is accompanied by an increase in the magnetic moment of the sample. In this case, the magnetization vectors of the Gd–Co(35 nm) and Co(7 nm) layers deviate from the direction of application of the external magnetic field. The appearance of this phase is shown schematically in Figure 2g,h(4). As a result, at $T > T^*$, the magnetization of the Co layers separated by the Cu layer ceases to be parallel, which leads to an increase in the resistance of the spin valve element (Figure 2a,c). An increase in the external field contributes to the alignment of the magnetic moments of all layers along the field direction. Thus, the magnetizations in the Co layers separated by a Cu layer turn out to be parallel again, which is accompanied by a decrease in the resistance of the spin valve element.
Figure 2. Magnetoresistance loops (a–f) for Gd-Co(35 nm)/Co(7 nm)/Cu(4 nm)/Co(7 nm) spin valve measured at different temperatures. (a,c,e) show low field part of MR hysteresis loops on enhanced scale. Schematic configurations of magnetic moments of pure Co layers as well as Co and Gd sublattices of the Gd-Co layer (g,h). At T > T*, the moment of Co total sub-network for Gd-Co(35 nm)/Co(7 nm) bilayer is larger than that of Gd sublattice of the Gd-Co(35 nm) layer (g), and vice versa at T < T* the magnetic moment of the Gd sub-lattice dominates over that of the Co sub-network (h).
4. Discussion

It is well known that in ferrimagnets, the critical field of the appearance of non-collinear structure can be expressed as follows: \( H_{cr} = J | M_1 - M_2 | \), where \( J \) is the exchange constant, \( M_i \) is the magnetization of i-sub-lattice. It follows from this expression that \( H_{cr} \) decreases when approaching a magnetization compensation temperature. This is also true for artificially layered Gd-Co(35 nm)/Co(7 nm) ferrimagnet designed for the present studies [19]. Therefore, it seems quite logical that for our sample, \( H_{cr} \) decreases when approaching \( T^* \) (Figure 2b,d and Figure 3). A decrease in \( H_{cr} \) is accompanied by an increase in the angle of deviation from the direction of the magnetization field of the Co layer in Gd-Co(35 nm)/Co(7 nm) bilayer. This increases the angle between the magnetizations in the Co layers separated by a Cu layer, which leads to a relative increase in the resistance of the spin valve (Figure 2b,d).

As noted above, at temperatures below \( T^* \), the magnetization in the Co layers separated by a Cu layer is arranged antiparallel to each other in a relatively small positive magnetic field. Therefore, the occurrence of a non-collinear phase and the gradual alignment of the magnetic moments of all layers leads only to a decrease in the resistance of the spin valve element (Figure 2h(3–5) and Figure 2f).

Changes in the chemical composition of the Gd-Co layer, its thickness, as well as the thickness of the Co layer will lead to changes in the magnetic properties of artificial layered ferrimagnet of Gd-Co/Co type [16,19]. Thus, it is possible to vary, within certain limits, the magnitude of the critical field of the onset of the non-collinear phase and the type of the MR(H) dependence in the range of the large fields.

![Figure 3](image)

**Figure 3.** VSM hysteresis loops for Gd-Co(35 nm)/Co(7 nm)/Cu(4 nm)/Co(7 nm) spin valve multilayered element measured at different temperatures: (a) 300 K; (b) 190 K; (c) 150 K.

Recently, special attention has been paid to the development of magnetic sensors capable to respond on the change of the temperature. Different physical effects were proposed for this kind detectors, including sensors deposited onto flexible substrates [20–22]. Based on the presented results, we can propose a two-stage object position sensor development as a contribution to the above-mentioned field. An abrupt change in resistance during the reversal of the spin valve in the range of small fields can serve as a trigger, and the change in resistance due to the emergence and evolution of the non-collinear phase in the range of the large fields can be the basis for precise determination of the position of the object. The simplest example is the angular control for rotation of the gear [23].

5. Conclusions

In the present work, magnetic and magnetoresistive properties of magnetic multilayered Gd-Co/Co/Cu/Co thermo-sensitive spin valve element were comparatively analyzed. It is shown that the appearance of a non-collinear magnetic structure significantly affects the parameters of the magnetoresistive hysteresis loop. Based on the presented results, a two-stage thin-film-type sensor can be developed for object position monitoring.
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References
1. Hartman, U. (Ed.) Magnetic Multilayers and Giant Magnetoresistance. Fundamentals and Industrial Applications; Springer-Verlag: Berlin, Germany, 2000; pp. 1–320. ISBN 978-3-642-08487-4.
2. Baibich, M.N.; Broto, J.M.; Fert, A.; Van Dau, F.N.; Etienne, P.; Creuzet, G.; Friederich, A.; Chazelas, J. Giant magnetoresistance of (001)Fe/(001)Cr magnetic superlattices. Phys. Rev. Lett. 1998, 61, 2427–2427. [CrossRef] [PubMed]
3. Dieny, B.; Speriosu, V.C.; Parkin, S.S.P.; Gurney, B.A.; Wilhoit, D.R.; Mauri, D. Giant magnetoresistive in soft ferromagnetic multilayers. Phys. Rev. B 1991, 43, 1297–1300. [CrossRef]
4. Freitas, P.P.; Leal, J.L.; Plaskett, T.S.; Melo, L.V.; Soares, J.C. Spin-valve structures exchange biased with a-Tho_{0.75}Co_{0.25} layers. J. Appl. Phys. 1994, 75, 6480–6482. [CrossRef]
5. Svalov, A.V.; Fernandez, A.; Tejedor, M.; Kurylandskaya, G.V. The effect of the additional biasing on the switching process in pseudo spin-valve structure. Vacuum 2007, 81, 1012–1015. [CrossRef]
6. Dieny, B. Spin valves. In Magnetoelectronics; Johnson, M., Ed.; Elsevier: Amsterdam, The Netherlands, 2004; pp. 67–150. ISBN 0-12-088487-9.
7. Parkin, S.S.P.; Hayashi, M.; Thomas, L. Magnetic Domain-Wall Racetrack Memory. Science 2008, 320, 190–194. [CrossRef] [PubMed]
8. Yang, D.Z.; You, B.; Zhang, X.X.; Gao, T.R.; Zhou, S.M.; Du, J. Inverse giant magnetoresistance in Fe/Cu/Gd_{1−x}Co_{x} spin-valves. Phys. Rev. B. 2006, 74, 024411. [CrossRef]
9. Jiang, X.; Gao, L.; Sun, J.Z.; Parkin, S.S.P. Temperature dependence of current-induced magnetization switching in spin valves with a ferrimagnetic CoGd free layer. Phys. Rev. Lett. 2006, 97, 217202. [CrossRef] [PubMed]
10. Bellouard, C.; George, B.; Marchal, G.; Maloufi, N.; Eugene, J. Influence of the thickness of the CoFe layer on the negative spin-valve effect in CoFe/Ag/CoFeGd trilayers. J. Magn. Magn. Mater. 1997, 165, 312–315. [CrossRef]
11. Bai, X.J.; Du, J.; Zhang, J.; You, B.; Sun, L.; Zhang, W.; Hu, A.; Zhou, S.M. Influence of the thickness of the FeCoGd layer on the magnetoresistance in FeCoGd-based spin valves and magnetic tunnel junctions. J. Phys. D Appl. Phys. 2008, 41, 215008. [CrossRef]
12. Lai, C.-H.; Lin, C.-C.; Chen, B.M.; Shieh, H.-P.D.; Chang, C.-R. Positive giant magnetoresistance in ferrimagnetic/Cu/ferrimagnetic films. J. Appl. Phys. 2001, 89, 7124–7126. [CrossRef]
13. Svalov, A.V.; Kurylandskaya, G.V.; Vas’kovskiy, V.O. Thermo-sensitive spin valve based on layered artificial ferrimagnet. Appl. Phys. Lett. 2016, 108, 063504. [CrossRef]
14. Milyaev, M.; Naumova, L.; Chernyshova, T.; Proglyado, V.; Kamensky, I.; Krinitsina, T.; Ryabukhina, M.; Ustinov, V. Magnetization reversal and inverted magnetoresistance of exchange-biased spin valves with a gadolinium layer. J. Appl. Phys. 2017, 121, 123902. [CrossRef]
15. Naumova, L.I.; Milyaev, M.A.; Krinitsina, T.P.; Makarov, V.V.; Ryabukhina, M.V.; Chernyshova, T.A.; Maximova, I.K.; Proglyado, V.V.; Ustinov, V.V. Microstructure and Magnetic Properties of the Gadolinium Nanolayer in a Thermo-Sensitive Spin Valve. Phys. Met. Metallogr. 2018, 119, 817–824. [CrossRef]
16. Vas’kovskiy, V.O.; Svalov, A.V.; Balymov, K.G.; Kurylandskaya, G.V.; Sorokin, A.N. Induced magnetic phase transitions in GdCo/Co-type multilayer films. Phys. Solid State 2008, 50, 1481–1486. [CrossRef]
17. López Antón, R.; Svalov, A.; Barandiarán, J.M.; Charlton, T.R.; Krzystyniak, M.; Kurylandskaya, G.V. Study of GdCo/Si/Co/Si multilayers by polarized neutron reflectivity. J. Phys. Conf. Ser. 2011, 325, 012018. [CrossRef]
18. Hansen, P.; Clausen, C.; Much, G.; Rosenkranz, M.; Witter, K. Magnetic and magneto-optical properties of rare-earth transition-metal alloys containing Go, Tb, Fe, Co. *J. Appl. Phys.* 1989, 66, 756–767. [CrossRef]

19. Andrés, J.P.; González, J.A.; Hase, T.P.A.; Tanner, B.K.; Riveiro, J.M. Artificial ferrimagnetic structure and thermal hysteresis in Gd$_{0.47}$Co$_{0.53}$/Co multilayers. *Phys. Rev. B* 2008, 77, 144407. [CrossRef]

20. Tehranchi, M.M.; Ghanaatshoar, M.; Mohseni, S.M.; Coisson, M.; Vázquez, M. Temperature dependence of magnetoimpedance in annealed Co-based ribbons. *J. Non Cryst. Solids* 2005, 351, 2983–2986. [CrossRef]

21. Bukreev, D.A.; Moiseev, A.A.; Derevyanko, M.S.; Semirov, A.V. High-Frequency Electric Properties of Amorphous Soft Magnetic Cobalt-Based Alloys in the Region of Transition to the Paramagnetic State. *Russ. Phys. J.* 2015, 58, 141–145. [CrossRef]

22. Nabias, J.; Asfour, A.; Yonnet, J.-P. Temperature Dependence of Giant Magnetoimpedance in Amorphous Microwires for Sensor Application. *IEEE Trans. Magn.* 2017, 53, 1–5. [CrossRef]

23. Prinz, G.A. Magnetoelectronics applications. *J. Magn. Magn. Mater.* 1999, 200, 57–68. [CrossRef]