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Correlation between Phase-Structural State and Magnetic Characteristics of Spin-Valve Systems Based on Fe, Co and Au

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This paper presents the results of investigation of phase-structural state, magneto-optical and magneto-resistive properties of multilayer spin-valve films structures on the basis of Fe, Co and Au. It was found that annealing of the samples up to $T_a = 600\text{-}720$ K leads to the formation of limited solid solution (s.s.) (Au, Co(Fe)) based on fcc-Au that considerably influences on the magnetic properties of the systems. The conditions and formation procedure of the most heat-stable systems with maximum values of magneto resistance, sensitivity to magnetic field changes and induction of demagnetization were found.

Keyword: Spin-valve structures, Demagnetization induction, Magnetoresistance, Kerr effect, Anisotropic magnetoresistance, Sensitivity.

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1. INTRODUCTION

The materials with spin-dependent electron scattering that obtain the phenomenon of giant magnetoresistance (GMR) are widely used in the sensor technology as the element base for magnetic storage of high-capacity, read heads, sensors of position and rotation, spin transistors and etc. [1, 2]. Magnetic properties of such systems are well studied, but there are some problems that need investigation: the temperature effect on phase-structural states and respectively on magnetic characteristics of these structures, since phase formation, recrystallization and diffusion processes can lead to changes in exchange interaction between the magnetic layers and break antiferromagnetic or ferromagnetic ordering [3, 4].

Spin-valves on the basis of Co and Au are widely spread as they have great values of magneto resistance (MR) [5]. However, how it shows in the [6], during annealing of such structures, a solid solution fcc-(Au, Co) is formed and the integrity of the nonmagnetic layer breaks. This process causes the disturbance of spin-dependent electron scattering. Systems with magnetic layers on the basis of Fe are more thermally stable [7]. That is why it was used as material of one of the magnetic layers. Besides systems that contain two ferromagnetic materials (FM) obtain the great saturation value of Fe layer and great anisotropy of Co layer [8-11]. Besides, the usage FM leads to formation of magnetic layers (ML) with different demagnetization induction (B_C). Such structures are called pseudo spin-valves (hereinafter referred to as spin-valve) because separate magnetic reversal of ML is obtained not with "pinned" layer, but with the variety of coercive forces that is achieved by using different materials and their thicknesses.

The layer condensation order influences on the isotropy of magnetic properties and the difference in coercive force values for systems on the basis of Fe and Co [9]. Furthermore, for these films various growth mechanisms on substrates are possible. Therefore, the condensation sequence of the spin-valve's ML can have a considerable influence on sample's magnetic characteristics. The purpose of this paper was to investigate the influence of annealing temperature, thickness, and sequence of ferromagnetic layers (FL) on the phase-structural state and magnetic properties of spin-valve structures.

2. EXPERIMENTAL

The research was carried out for four types of spin-valves structures with different sequence and thickness (in nanometers) of ML:

I – Au(3)/Co(3)/Au(6)/Fe(20)/Sub,
II – Au(3)/Fe(20)/Au(6)/Co(3)/Sub,
III – Au(3)/Fe(3)/Au(6)/Co(20)/Sub,
IV – Au(3)/Co(20)/Au(6)/Fe(3)/Sub.

The film thickness was chosen in the way so that the "soft magnetic" layer was ≈ 16 % from the thickness of the "hard magnetic" layer (3 and 20 nm were accepted) [12]. Nonmagnetic layer should be thick enough to prevent the appearance of shift field that occurs because of the interaction between FL through defects in interlayer and magneto-static connection caused by interface inequalities. The optimum thickness of Au layer is 5-7 nm [13]. In this case, separate magnetization of Fe and Co ML will be implemented. With increase in thickness of the layer (d_{Au}), volume scattering of electrons increases, leading to a substantial weakening of the exchange interaction between the layers.

Samples were condensed in the vacuum chamber at the pressure of residual atmosphere $7 \cdot 10^{-8}$ Pa on SiO_2/Si substrates. Before films formation, the substrates were cleaned by ultrasonic in acetone and annealed at the temperature of 770 K during 30 min in a vacuum $7 \cdot 10^{-8}$ Pa. Condensation rates were chosen in the way to eliminate the mixing of layers: $\omega_{\mathrm{Co,\,Fe}} = 0.3$ nm/min, $\omega_{\mathrm{Au}} = 0.9$ nm/min. Spin-valves were then covered with Au layer ($d \cong 3$ nm) to prevent oxidation on the atmosphere.

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Film thickness during condensation was controlled by quartz crystal. Then the samples were annealed in the vacuum chamber at the temperatures of 450, 600 and 750 K during 30 minutes for each value.

Phase-structural state of the samples was studied with the help of transmission electron microscopy, energy dispersive X-Ray analysis (EDAX) and ellipsometer methods. For spin-valves' magnetic characteristics analysis the magnetoresistance (MR) measurements were carried out in three geometries at different rotation angles of samples relative to the magnetic field lines (angle φ) and magneto-optical Kerr effect (MOKE) in longitudinal geometry at different rotation angles of samples in the surface plane (angle α).

3. RESULTS ANALYSIS

The studying of the samples using EDAX method showed that there were peaks only for Fe, Co, Au, Si and O (from substrate SiO_2/Si), that proved the absence of impurities in the systems (Fig. 1).

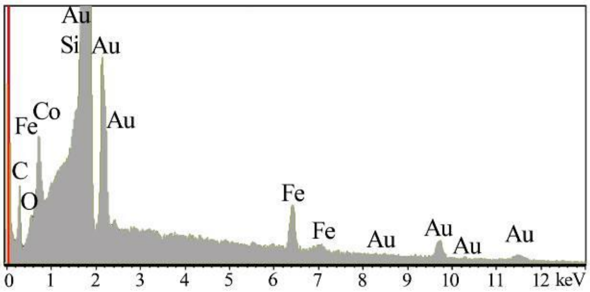


Fig. 1 – EDAX – spectra for Au(3)/Fe(20)/Au(6)/Co(3)/Sub

3.1 Spin-valve Phase-structural State

To establish the correlation between phase-structural state and the magnetic characteristics of spin-valves structures microscopic and ellipsometer study were carried out. They showed that all fresh condensed films retained individuality of their layers. After annealing up to $T_a = 600$-750 K solid solutions (s. s.) on the basis of Au fcc lattice (Au, Co(Fe)) were formed (Table 1).

It is possible to distinguish the lines that correspond to s.s. (Au, Co) or (Au, Fe) by estimating the standard deviation of the lattice parameter from the tabular data (Δa). Since the lattice parameter a(Au) = 0.4078 nm, and the parameters a(γ-Fe) = 0.3637 nm and a(fcc-Co) = 0.3554 nm, it can be stated that the lines that have got smaller values of Δa correspond to s.s. (Au, Fe). The calculations of lattice parameters for spin-valves of II-nd, III-rd and IV-th types indicate the valves, i.e. in those samples that have thicker Co layer.

The s.s. parameter Δa has the lowest value for the system of II-nd type, that indicates the prevalence of s.s. (Au, Fe).

Low-temperature phase Co (hcp-Co) was observed for all fresh condensed samples. During the annealing to 600 K, considerable thermal diffusion of Co atoms into nonmagnetic layer is going on, that causes the destruction of the long-range ordering in Au volume and formation of s.s. [14]. After samples cooling, hcp-Co grains are formed and cause the appearance of reflections on the diffraction patterns (Fig. 2e).

Microscopic studies have shown that after annealing of spin-valves to 600 K, s.s. are formed that lead to integrity violation in the layers. Only the III-rd system – Au(3)/Fe(3)/Au(6)/Co(20)/Sub maintains two separate ML, that explains its largest and most thermo-stable values of MR and sensitivity to magnetic field (p. 3.3).

Ellipsometer studies prove the phase composition of the spin-valves structures at different annealing temperatures that were experimentally determined by transmission electron microscopy (Fig. 3). Empirical dependences of azimuth and phase shift of the polarized light on the annealing temperature ($\Psi(T_a)$ and $\Delta(T_a)$ correspondingly) indicate the change in phase composition of the system after annealing to 600 K (Fig. 3a). Solving the inverse ellipsometry equation gives the possibility to compute the optical parameters (n, k) of each layer of spin-valves structure at different T_a. Fig. 3b presents the comparative analysis of the tabular data (solid line) and computed (dashed line) values of n (square mark) and k (triangle mark) for each material for the structure of II-nd type.

To solve the inverse ellipsometry problem the model structure with determined sample layers was simulated in specific software [12].

After annealing to $T_a = 600$ K, the computed optical parameters began rapidly deviate from tabular data. This fact indicated incorrect choice of structure theoretical model for solving the ellipsometry inverse problem.

After including of intermediate layers (s. s.), the structure model was correct and the computed values of n and k at $T_a = 600$ and 720 K were in good agreement with tabulated data (Fig. 3b). But the values of optical parameters for Fe, Co and Au layer are slightly different from tabular data for bulk samples at temperature 300 K.

Table 1 – Phase composition of spin-valves structures

T_a, K Structure	300	450	600	750
II	Au bcc-Fe hcp-Co	Au bcc-Fe hcp-Co	s.s. (Au,Fe(Co)) bcc-Fe hcp-Co (trace)	s.s. (Au,Fe(Co)) bcc-Fe
III	Au bcc-Fe hcp-Co	Au bcc-Fe hcp-Co	s.s. (Au,Co(Fe)) bcc-Fe hcp-Co	s.s. (Au,Co(Fe)) bcc-Fe (trace) hcp-Co
IV	Au hcp-Co bcc-Fe	Au hcp-Co bcc-Fe	Au s.s. (Au,Co(Fe) hcp-Co	s.s. (Au,Co(Fe) hcp-Co fcc- Co

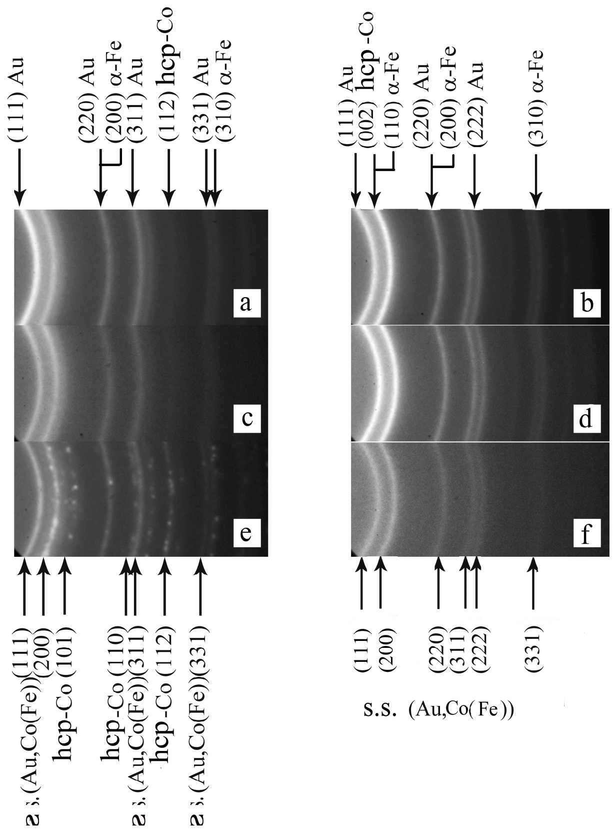


Fig. 2 – Diffraction patterns of the spin-valves structures of III-rd and IV-th types after annealing to 300 K (a, b), 600 K (c, d), 720 K (e, f)

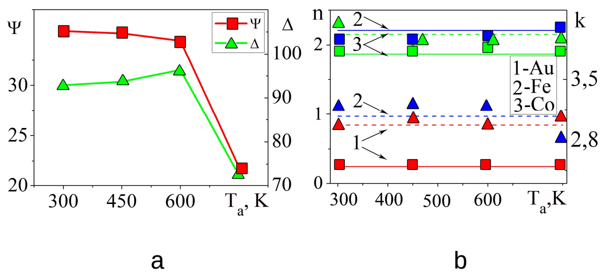
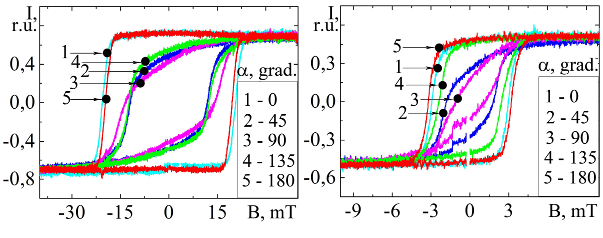


Fig. 3 – Ψ and Δ temperature dependences (a); tabular (lines) and computed (marks) data of optical parameters (*n* – square marks and solid lines, *k* – triangle marks and dashed lines) for Au, Co, Fe layers (b) of the spin-valve structure of II-nd type.

3.2 Magneto Optical Kerr Effect

The results of MOKE research for all spin-valves structures without annealing showed no shift field that indirectly indicates the integrity of non-magnetic layer. All samples showed magnetic anisotropy during rotation on angle α (in sample's plane). Thus, Fig. 4 presents MOKE – curves of the spin-valves structures of II-nd and III-rd types at different rotation angles (α).

Fig. 4 shows that the II-nd type structure has five times greater demagnetization induction value in comparison to III-rd type structure, although Co is more "hard magnetic" material than Fe and the sample with thicker Co layer ($d = 20$ nm) should have greater B_C value. This peculiarity is explained by the fact that as a result of quantum oscillations of interface and surface energies during thin film growth (transition metals in particular), there is a transformation from layer by layer to island-growth mechanism and back, that causes the fluctuation of B_C [15]. The authors of [15] explain the non-monotonic dependence of coercitivity on Co film thickness (under the same conditions of samples formation as ours) by the fact that at the effective thickness of 1.5 nm Stranski-Krastanow growth mechanism is realized when three-dimensional islands grow on two-dimensional layer. In this case the samples obtain greater roughness and imperfection that prevents the motion of domain walls and increases system's demagnetization induction. With further thickness raise, Co clusters are destroyed or become smaller, that reduces their roughness. When the film thickness is $d = 17$ nm minimum values of roughness and coercitivity are observed. Then Co layer grows layer by layer and the domain walls thickness gradually increases with monotonic increase in B_C. Therefore film coercive force with $d = 3$-4 nm is several times greater than that with $d = 17$-20 nm. Transition metals layers that are formed on the non-magnetic Au layer grow like "terraces" and have much lower roughness values than the ones that growth on the substrate [1]. The investigation of the spin-valves structures with atomic force microscopy showed that both systems have the same roughness of the upper layer: $\sigma = 2.4$ nm. This fact shows that during condensation of Co and Fe films on Au, they do not have such a non-monotonic $B_C(d)$ dependence like it appears during the growth on amorphous substrate. The above experimental results analysis let us explain the difference between demagnetization induction for structures of II-nd and III-rd types.



a b

Fig. 4 – MOKE – curves of spin-valves of II-nd and III-rd type

Fig. 5 shows $B_C(\alpha)$ dependence in polar coordinates of the four spin-valve types that were measured after annealing to different temperatures.

Spin-valves structures of II-nd and IV-th types have the greatest B_C value due to presence of thin ($d = 3$ nm) Co and Fe layers deposited on the substrate. Fig. 5 indicates that the spin-valves structures of I-st and III-rd types switch easier since thicker ($d = 20$ nm) and that's why less defective ML was condensed on the substrate first. In this case, the greatest demagnetization induction value has the structure of II-nd type.

After annealing to $T_a = 450$ K B_C decreases for all samples. This is connected with healing of film's defects, and following improvement of their domain structure [11]. With further temperature raise to $T_a = 600$ K demagnetization induction decreases for the structures of II-nd and IV-th types. The possible reason for this is interaction of FMs with the substrate and formation

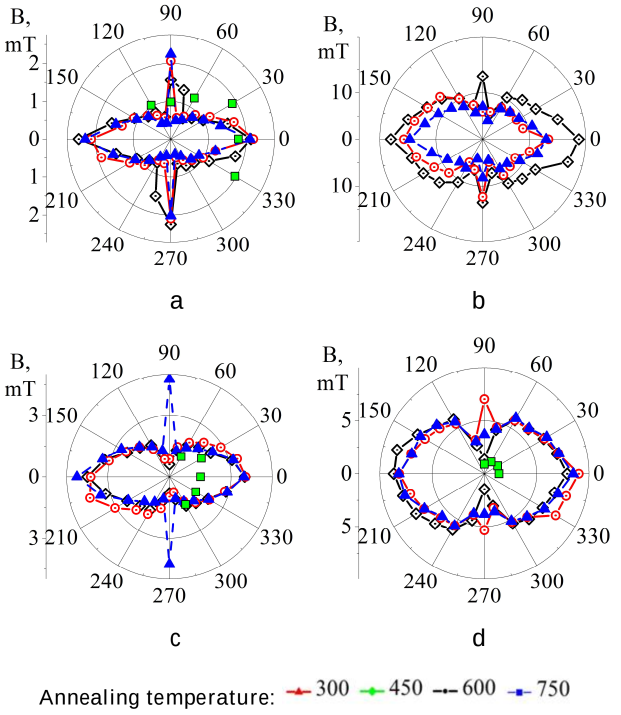


Fig. 5 – B_c dependences on rotation angle of the sample (α) in polar coordinates for systems: I (a), II (b), III (c), IV (d)

of silicides – thin non-magnetic layers, or oxides. X-ray studies did not allow locking the lines from the spin-valve lower layers, maybe because of insufficient sensitivity of this method. For other two systems, the B_C value increases. This fact may be related to increase of electron scattering on phonons with spin rotation that reduces the ML interaction. After annealing of spin-valves of III-rd (Fig. 5c) and IV-th types to $T_a = 600$°K (Fig. 5d), $B_C(\alpha)$ dependence behavior is changed, that indirectly indicates the phase formation in the systems. Most likely this is due to thicker ($d = 20$ nm) Co layer, that after annealing to 600 K forms limited s. s. (Au, Co). S. s. contribution to general B_C value is greater for the structures that has thicker Co layer.

Fig. 6 presents the dependency of samples' saturation field (B_S) on the T_a.

The above graph shows that samples which have thicker FL condensed on the substrate are easily saturated but have non-monotonic $B_S(T_a)$ dependence. The structure of II-nd type obtains the highest and most thermally stable value of the saturation field. Besides it has the maximum value of B_C. This fact indicates the antiferromagnetic relation of the MLs and can take place during the giant magneto resistance effect (GMR) [4]. Fig. 6 shows that after annealing to $T_a > 600$°K, the saturation field value rapidly grows.

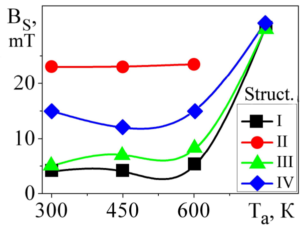


Fig. 6 – B_S temperature dependencies for all structure types

This situation can occur when structure of ML is changed. In particular, as a result of thermal diffusion of Co atoms into Au layer limited s. s. is formed. It "blurs" cobalt FL and prevents domain walls motion. There is no formation of new magnetic structure because the transition to paramagnetic state for Fe and Co is possible only at temperature $Ta > 1000$ K (Curie temperature for Fe).

3.3 Magnetoresistive Properties

While investigating MR properties it was found that all films except for the II-nd type ones have magnetic anisotropy. The MR greatest value is observed for spin-valves of III-rd type but MR has a different sign in the longitudinal and transverse measurement geometries. Furthermore, experimental results show that increase in the sample rotation angle (φ) leads to monotonic increase of MR and reaches its maximum at $\varphi = 60$-70°. Unequal MR values at different angles between the current flow direction and the magnetic field lines are explained by the advantages of different electron scattering mechanisms and different Lorentz force influence.

With the raise in annealing temperature, MR does not monotonically decrease for all samples (Fig. 7). The spin-valves structures of III-rd and IV-th types: Au(3)/Fe(3)/Au(6)/Co(20)/Sub, Au(3)/Co(20)/Au(6)/Fe(3)/Sub are the most thermally stable, their MR significantly changes only when $T_a > 700$ K (Fig. 7b). Most likely, at this moment the s. s. (Au, Co) is formed.

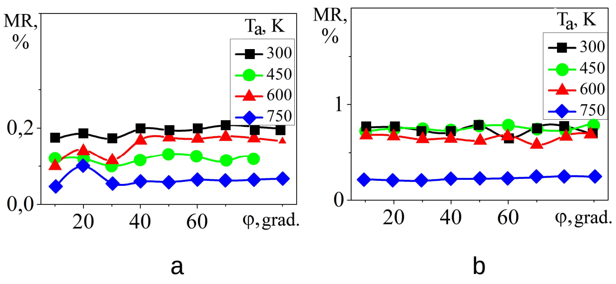
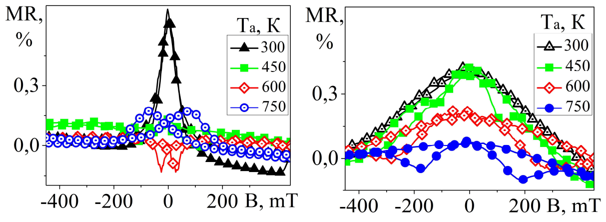


Fig. 7 – MR angular dependencies during transition from perpendicular to transversal measurement geometry at different T_a of II-nd (a) and III-rd (b) types structures

The MR of spin-valves of III-rd and IV-th types in perpendicular measuring geometry changes its sign and dependency behavior at different annealing temperatures (Fig. 8). This probably may be caused by the phase formation process. The appearance of s. s. (Au, Co) leads to decrease of thickness of the solid non-magnetic layer and correspondingly to changes in the interference of electron waves that are reflected from the interfaces. This phenomenon changes the indirect exchange relationship between FLs [4]. This means that during annealing process the transitions from antiferromagnetic to ferromagnetic interaction of ML happens. Initially (at $T_a = 300$ K and $d_{Au} = 6$ nm) anisotropic magnetoresistance (AMR) took place and demagnetization induction value was the smallest. With increase of temperature to 450 K there was a transition to isotropic MR (it has the same sign in perpendicular and longitudinal measurement geometry) and a dramatic increase in B_C, that indicates the antiferromagnetic relation of ML. With further anneal ing, MR changes its sign again.



a b

Fig. 8 – MR of III-rd and IV-th types spin-valves in perpendicular measurement geometry after annealing of the samples to different T_a

In particular, recrystallization and diffusion processes in the non-magnetic layer caused integrity violation elimination of spin-dependent scattering effect of conductive electrons and led to AMR [15].

Such changes in indirect exchange relationship took place only in spin-valves with relatively thick Co layer: Au(3)/Fe(3)/Au(6)/Co(20)/Sub, Au(3)/Co(20)/Au(6)/Fe(3)/Sub (III-rd and IV-th typed). This phenomena is explained by the fact that greater amount of Co atoms is involved in formation of limited s. s. with Au and essential changes in thickness of solid non-magnetic interlayer.

This way only Au(3)/Fe(20)/Au(6)/Co(3)/Sub spin-valve structure has MR isotropy at three measurement geometries, the greatest and most thermally stable value of the saturation field. Au(3)/Fe(3)/Au(6)/Co(20)/Sub system has the greatest and most thermally stable value of MR but it also has variable type of indirect exchange interaction of FL.

Appearance of "steps" on the MR graphs for spin-valves structures after annealing to definite temperatures (Fig. 9 – arrow marked) is the indication of heterogeneity of FL and indirectly points to structural changes in ML (e.g., s. s. appearence).

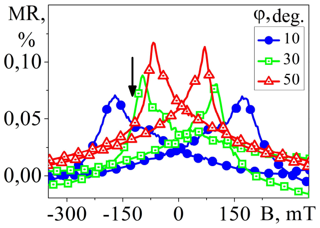


Fig. 9 – MR in longitudinal measurement geometry for Au(3)/Fe(20)/Au(6)/Co(3)/Sub system after annealing to $T_a \cong 750$ K and different rotation angles (φ)

One of the most important peculiarities while choosing the materials for sensor development is their sensitivity to changes in magnetic field (S). For all spin-valves structures the S values were obtained on the basis of MR curves at different measurement geometries and annealing temperatures (Table 2).

As we can see from the table after annealing the sensitivity of all structures except for Au(3)/Co(3)/Au(6)/Fe(20)/Sub decreases. Au(3)/Fe(3)/Au(6)/Co(20)/Sub spin-valve structure has the greatest S values at all measurement geometries and annealing temperatures.

Table 2 – Spin-valves' sensitivity to magnetic field changes (S,% / T)

Geometry	Perpendicular				Longitudinal				Transversal			
T_a, К	300	450	600	750	300	450	600	750	300	450	600	750
I	< 0.11	0.36	0.17	–	0.07	–	0.21	0.19	0.33	0.46	0.97	0.41
II	< 0.07	< 0.08	< 0.09	0.09	< 0.34	< 0.28	< 0.34	< 0.24	< 0.43	–	< 0.32	0.17
III	5.02	0.06	1.06	0.48	4.33	0.45	< 0.34	0.43	10.65	15.73	7.27	2.39
IV	< 0.90	< 0.91	< 0.44	< 0.15	–	–	–	–	8.29	–	10.74	7.76

4. CONCLUSIONS

The investigation of phase-structural state of the spin-valves structures on the basis of Fe, Co and Au showed that all fresh condensed films retain the individuality of their layers. After annealing to 600 K s. s. (Au, Fe) and s.s. (Au, Co) are formed in spin-valves. Ellipsometer studies proved the obtained results and let us define the optical parameters of spin-valve layers at different annealing temperatures. The investigation of MOKE and MR properties of all four spin-valve structures types gave such results:

1) It was found that systems that have thick Co ($d \cong 20$ nm) layer as "hard magnetic" one have the greatest and most stable MR values. But they have anisotropy in longitudinal and transversal measurement geometries (MR has different signs). Besides at perpendicular geometry MR changes its sign at different annealing temperatures. This can be explained by the fact that the formation of s. s (Au, Co) leads to decrease in solid non-magnetic layer thickness and causes the oscillation in indirect exchange relationship between MLs, i.e. there are transition from antiferromagnetic to ferromagnetic interaction of MLs. Spin-valves that have relatively thick Co layer have greatest sensitivity to magnetic field at all measurement geometries and annealing temperatures too.

2) It was found that systems with relatively thick Fe layer ($d \cong 20$ nm) as "hard magnetic" one in spin-valves have the greatest and most thermally stable values of saturation and demagnetization inductions. Besides MR dependencies for these spin-valves is isotropic at three measurement geometries and retain their sign during changes of annealing temperature.

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