Thin Film Systems Based on Co and Cr Or Cu: Magnetoresistive Properties and Application

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Abstract This article is presented the magnetoresistive properties and detailed examination of phase state and crystal structure on the as-deposited and heat-treated thin film systems Co/Cr/Co and Co/Cu/Co. In this systems observed two different types of structures (multilayer and granular film), which can be used as sensing elements of magnetic sensors.

Keywords Thin Film, Solid Solution, Magnetoresistance, Magnetic Anisotropy, Coercivity, Sensitivity

1. Introduction

Magnetic sensors based on GMR effect characterized by quick response under low magnetic field, high sensitivity, capable of measuring high magnetic fields and not the least of the factor small size and low cost etc. Thus they have great potential for application in different fields: magnetic imaging, biosensor, contactless position detection, as reading heads in computer hard drives [1-4]. As sensing element of such sensors based on different types on thin film systems such as: structure which consist of two magnetic layers separated with non-magnetic layer; granular structures where ferromagnetic metallic nanoparticles embedded at non-magnetic metallic matrix or spin-valves consist of two magnetic layers, one of thus is fixed and another one is free, which separated with nonmagnetic layer (for fixing one of magnetic layers added antiferromagnetic layer to the top or bottom part of structure).

Today, the nanosize structures based on such magnetic materials as Co or Fe in aggregate with non-magnetic materials like Cr, Cu, Ag Au etc. use extensively at formation of all types of structures listed above [5-8].

In this article, the magnetoresistive properties and probable field of application for two types of structures were investigated: three-layer structure on the base of Co and Cr and granular films based on Co and Cu. Besides, we discuss the influence of the thicknesses or concentration on its properties, important from the application point of view.

2. Experimental methods

Thin film systems of both types were prepared by method of layer by layer condensation (e-beam evaporated) on sital substrate (S) in high vacuum system ($p \sim 10^{-4}$ Pa) with average rate $\omega = 1,2 - 4,8$ (Co) and $0,6 - 1,8$ nm/min (Cr, Cu). The Ag layer of 5 nm was deposited on the top samples as protective coating. The silicon was used as a substrate material because it meets the following requirements: dielectric, temperature-stable, low coefficient of thermal expansion, the 14th class of surface roughness and high mechanical strength. The substrate temperature was $T_s = 460$ K for better adhesion films to the substrate. Besides, this also gets you closer structurally perfect samples with less crystal defects. The electrical contacts on the base of two-layer systems Ag/Cu was formed on the top of substrate before thin film systems preparation. The Cu bottom layer of 100-150 nm was used as auxiliary layer and Ag top layer of 30 nm, which characterized by high inertness and conductivity, was used as contact layer.

Figure 1. The structures of two types of samples, which were used at investigation: I – multilayer systems; II – granular films

Thus two series of samples were prepared: (I) three layer systems Co(5)/Cr(d_{Cr})/Co(20)/S (the thicknesses of top and bottom layers of Co remain constant and the thickness of Cr layer changes in the range from 3 to 20 nm); (II) three layer systems Co/Cu/Co/S atoms on basis of which granular structures have been prepared (the common concentration of Co atoms was equal $c_{Co} = 62-88$ at.%). The schematic

structures of two types of samples are presented at Fig.1.

The study of magnetoresistive properties was carried out with using software-hardware complex with current-in-plane geometries in an external magnetic field from 0 до 500 mT at room temperature according the methods, which describe at work [9]. The measurement of magnetoresistance (MR) was carried out in three geometries: perpendicular, transverse and longitudinal. The value of magnetoresistance has been calculated as

$$MR = \frac{(R(B) - R(B_s))}{R(B_s)} \cdot 100\%,$$

where $R(B)$ and $R(B_s)$ are resistance of thin film samples at a given and saturated field respectively.

To study the effect of temperature on phase state, structural characteristics and magnetoresistive properties of thin film samples the heat treatment was carried out to annealing temperatures $T_a = 700$ or 800 (to analyze the effect of the phase transition $hcp-Co \rightarrow fcc-Co$, which occurs at 690 K, on magnetoresistive properties) and 1000 K (influence of temperature on the stability of sensitive elements, which can be made on the base of the chosen film systems). The annealing duration carried out by the scheme «heating $\rightarrow$ excerpt for 20 min $\rightarrow$ cooling to room temperature» with using the computerized complex, which described at work [10].

Structural and phase state investigation were made by using TEM and diffraction measurements on the transmission electron microscope TEM-125K.

2. Experimental Results

In earlier studies have repeatedly stated that the creation of effective sensing elements based on the type of structures $Me_1/Me_2/Me_1/S$ is necessary to conduct comprehensive studies of magnetoresistive properties, structural and phase state. The detailed analysis of the phase state and the crystal structure film systems showed the following. The phase state of film systems $Co/Cr/Co/S$ after condensation corresponds to $bcc-Cr + hcp-Co$ and crystalline structure has nanoscale character. The diffraction lines $d111$ and $d200$ from $fcc-Co$, which observed at room temperature (Fig. 2a), are not associated with the formation of $fcc-Co$ crystallites as a result of the phase size effect, and with formation of stacking faults at $hcp-Co$ (low temperature phase) as well as in bulk samples [11]. After annealing to 800 K the change of phase composition does not occur, there is only a slight increase of crystallite size. At $T_a \geq 900$ K the thin film Cr almost completely oxidized to the composition of Cr_2O_3 (Fig. 2c). Thus, dependences, which presented at Fig. 4, described the magnetoresistive properties of system $Co/(bcc-Cr + Cr_2O_3)/Co/S$.

In the case of systems based on Co and Cu has place the formation of solid solution (Co, Cu) on the base of Cu fcc lattice at a condensation stage. The annealing to 700 K

occurs to polymorphic transition $hcp-Co \rightarrow fcc-Co$. Partial disintegration of solid solution with formation granules of Co in solid solution matrix occurs at annealing to 850 K (the diffraction rings of $hcp-Co$ fixed at electron-diffraction pattern (Fig. 3c)). Thus the purpose of formation granular films was attained.

Figure 2. Diffraction pattern (a-c) and crystalline structure (d, e) of film systems $Co(5)/Cr(5)/Co(20)/S$ as deposited (a, d) and after annealing to $T_a = 800$ K (b), 1000 K (c, e)

Figure 3. Diffraction pattern (a-c) and crystalline structure (d, e) of film systems $Co(22)Cu(17)Co(20)/S$ as deposited (a, d) and after annealing to $T_a = 700$ K (b), 850 K (c, e)

Fig. 4 and 5 shows the magnetoresistance curves after condensation and heat-treated typical of the $Co/Cr/Co/S$ and $Co/Cu/Co/S$ systems. The results of calculation of MR value and coecivity are presented in Table 1. The characteristic properties of this data are following. The magnetoresistance effect in film systems $Co/Cr/Co/S$ (Fig. 4) characterized by not great value of MR ($0.1-0.3\%$), here with maximum value 0.4% obtained in perpendicular geometry after heat treated to 800 K at the thickness of interlayer $dCr = 20$ nm. In

addition, sensing elements on the base of Co and Cr attributed by sufficiently large values of coercivity B_c (> 100 mT) at Co atom concentration $c_{Co} = 56\text{--}63$ at.% in perpendicular geometry as after condensation so as after heat treated to 800 K. At increasing c_{Co} take place decreasing of B_c value. Though, it should be noted that at high-temperature annealing to 1000 K observed significant increasing of coercivity for all range of concentration and all types of measurement geometries. For example, for film system Co(5)/Cr(13)/Co(20)/S the value of B_c increases from 23 (300 K) to 200 mT (1000 K) in perpendicular geometry. The increasing of coercivity as a result of phase state changing of sample.

Figure 4. Magnetoresistance dependence versus applied field for film systems Co(5)/Cr(5)/Co(20)/S (a, c, e) and Co(5)/Cr(13)/Co(20)/S (b, d, f) after condensation (a, b) and heat treated to 800 K (c, d) and 1000 K (e, f). Magnetic field lying in perpendicular (1), longitudinal (2), transverse (3) geometries

Thus at work [5] has been reported that the in-plane coercivity can be increased by thermal treatment from 1 to 24 mT. According to work [5] structural and magnetic properties of structures based on Co and Cr are good candidate for using as sensing elements of magnetic sensors and as hard spin injectors. Peculiarity of hysteresis of field dependence is availability double peak (see, for example, magnetoresistance dependence vs. applied field for film system Co(5)/Cr(13)/Co(20)/S (Fig. 4b, d, f). It's can be explained by alternate magnetic reversal of Co layers [12]. It should be noted, that for film systems Co/Cr/Co/S in all range of interlayer thickness take place anisotropy of magnetoresistance at transfer to longitudinal geometry of measurement. The value of anisotropy increases at decreases of magnetic component atom concentration.

The value of the magnetoresistance for structures of second type depends of total concentration of Co atom and changes from 0.2 to 0.4% at increasing c_{Co} from 60 to 87 at.%. Besides, magnetoresistive properties of granular films based on Co and Cu slowly depend on heat treated. The annealing to 700 K leads to slight decrease of the values of MR and saturated field B_s . At the same time heat treatment of samples Co(14)/Cu(9)/Co(14)/S (Fig. 5d) reduces to decrease of the magnetoresistance effect in the perpendicular geometry and its increase in other geometries. The value of B_s changes in a similar way (from 140 to 24 mT – in the perpendicular and from 35 to 39 mT – in longitudinal geometry).

Figure 5. Magnetoresistance dependence versus applied field for film systems Co(14)/Cu(7)/Co(14)/S (a, c) and Co(14)/Cu(9)/Co(14)/S (b, d) after condensation (a, b) and heat treated to 700 K (c, d)

In forming the structure of the sensing element of considerable importance is the ability of the sensor to respond to changes in the magnetic field irrespective of measurement geometry and the value of the sensitivity to the magnetic field (S_B). Depending on the application, the sensor sensitive element should have high sensitivity and to provide a rapid response to changes in sensor input signal (e.g., instantaneous closure / opening of the circuit in automation) or medium in order to be able to provide high accuracy of measurement the detection of weak fields.

The maximum value of the sensitivity of the film system to the magnetic field was determined by the equation $(\Delta R/R(B_s))_{\max}/\Delta B$. The results of S_B calculations for the samples of both types after condensation and heat treated are presented in Table 2.

The highest value of magnetic sensitivity for film systems based on Co and Cr for a sample of Co(5)/Cr(20)/Co(20)/S is 19.8 %/T in the perpendicular geometry of the measurement; for film systems based on Co and Cu for a sample of Co(14)/Cu(9)/Co(14)/S – 21.5%/T in the transverse geometry of the measurement. Note that those structures can be used in analog and digital circuits for fast response to changing magnetic flux.

Table 1. The value of MR and coercivity (B_c) for film systems of both types after condensation and heat treated

Film system	c_{Co} , at. %	T , K	MR, %			B_c , mT		
			measurement geometry			measurement geometry		
			perpend.	transverse	longitud.	perpend.	transverse	longitud.
Co(5)/Cr(5)/Co(20)/S	83	300	0.18	0.06	-0.03	23.06	13.21	32.62
		800	0.21	0.14	-0.06	90.74	13.51	20.39
		1000	0.10	0.15	-0.04	199.72	49.69	52.25
Co(14)/Cu(7)/Co(14)/S	81	300	0.19	0.30	0.26	140	29	35
		700	0.22	0.27	0.22	24	37	39
Co(14)/Cu(9)/Co(14)/S	77	300	0.24	0.30	0.21	200	14	30
		700	0.20	0.37	0.27	134	37	44
Co(5)/Cr(10)/Co(20)/S	71	300	0.13	0.04	-0.02	12.53	17.00	15.18
		800	0.22	0.12	-0.01	26.92	13.31	22.13
		1000	0.08	0.13	-0.03	183.96	72.15	42.18
Co(20)/Cu(25)/Co(25)/S	66	300	0.34	0.26	0.26	100	35	37
		700	0.25	0.26	0.25	100	22	39
Co(5)/Cr(15)/Co(20)/S	63	300	0.19	0.13	-0.04	129.55	13.96	21.04
		800	0.27	0.20	-0.10	149.66	16.57	20.16
		1000	0.04	0.06	-0.02	67.98	54.01	73.02
Co(5)/Cr(20)/Co(20)/S	56	300	0.26	0.10	-0.06	139.47	16.06	15.75
		800	0.40	0.16	-0.07	20.16	15.21	17.93
		1000	0.02	0.02	0.03	117.22	37.12	67.49

Table 2. The value of S_B for film systems of both types after condensation and heat treated

Film system	c_{Co} , at. %	T , K	S_B , %/T		
			measurement geometry		
			perpendicular	transverse	longitudinal
Co(5)/Cr(5)/Co(20)/S	83	300	7.8	4.5	0.9
		800	10.0	10.4	3.2
		1000	0.5	3.0	0.8
Co(14)/Cu(7)/Co(14)/S	81	300	1.3	10.1	7.3
		700	9.3	7.3	5.7
Co(14)/Cu(9)/Co(14)/S	77	300	1.2	21.5	6.9
		700	1.5	10.1	6.1
Co(5)/Cr(10)/Co(20)/S	71	300	1.1	2.4	1.2
		800	8.2	9.0	0.2
		1000	0.5	1.8	0.7
Co(20)/Cu(25)/Co(25)/S	66	300	3.4	7.5	7.0
		700	2.5	11.8	6.5
Co(5)/Cr(15)/Co(20)/S	63	300	10.4	9.3	1.7
		800	18.7	12.0	4.9
		1000	0.5	1.1	0.2
Co(5)/Cr(20)/Co(20)/S	56	300	6.2	6.2	3.8
		800	19.8	10.5	3.9
		1000	0.1	0.5	0.4

Analysis of the data for the other samples also allows identifying possible areas of application of the magnetic field sensor based on them. Since the sensitivity to magnetic field, in most cases not exceeding 10%/T, such a structure is more suitable for detection of weak magnetic fields.

3. Conclusions

The results of investigation of phase state of thin film system of two types show that the samples based on Co and Cr has two-phase state and in the samples based on Co and Cu the take place formation nanostructured solid solution with granules of Co. So the first one of systems allows realizing the multilayer structures and second one – granulated structures for production sensing elements of magnetic field sensors. Notes, both types of systems depending on the concentration of components can be used in analog and digital circuits for rapid response to changing magnetic flux or when creating a stable sensor for detecting weak magnetic fields. Besides, the phase states of systems slowly depend on heat treated to 800 K, it allows to exclude the influence of temperature on the working characteristics of the sensors.

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