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Effect of annealing and additive agent on magnetoresistance properties of pulse plated Cu–Co nano-granular alloys

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ABSTRACT

In this report, magnetization and magnetoresistance properties of pulse (PC) and direct current (DC) deposited Cu–Co alloy films containing 37 at.% of cobalt and higher were investigated. Magnetization measurements revealed, even at high cobalt content, the co-existence of superparamagnetic (SPM) nano-granules along with FM regions. Addition of saccharine within the electrolyte led to a reduction in the coercivity of the films but annealed samples had opposite effect on it. Room temperature magnetoresistance (MR) measurements showed resistance change due to anisotropic magnetoresistance (AMR) of the as-deposited films. Upon annealing, several times increase of MR was noticed with the appearance of typical giant magnetoresistance (GMR) behavior. A maximum negative GMR of 3.2% was obtained for annealed pulse plated $Cu_{62.5}Co_{37.5}$ alloy film. For DC plated samples, addition of saccharine had noticeable effect on GMR compared to PC plated alloys.

1. Introduction

Research on magnetoresistance and magnetoresistive materials by physical deposition techniques is quite matured enough and has laid the foundations of spintronics [1]. Most extensive studied materials are either magnetic metallic multilayers or alloys. Among the various available deposition techniques, electrodeposition has long been considered as a feasible alternative to the expansive vacuum methods for magnetic multilayer preparation [2,3] because of its cost-effectiveness. Advancements in electrochemical science and technology for the last one and half decade, makes possible to synthesize the high quality metallic multilayers even with sublayer thickness of 1 nm or less [2]. In spite of these efforts, many application-relevant parameters especially magnetic field sensitivity, have still remained inferior compared to its vapor deposition counterparts. This fact has actually motivated, until now, the continuous research efforts in this particular field [2,4–9]. These materials find potential applications in magnetoresistive heads, magnetic RAM's, magnetic storage devices and various low end applications [2,10–14].

Out of several multilayer systems exhibiting giant magnetoresistance (GMR), Co/Cu multilayers have been studied quite extensively in the past few years [2,4–9,15–17]. Besides Co/Cu multilayers, granular Co–Cu alloys [18–22] and granular multilayers [2,23] also exhibit GMR. Granular multilayers consisting of layers of grains of ferromagnetic material separated by layers of normal metal, is a border between the granular alloys and the multilayers. These are sometimes preferred due to their fully isotropic magnetoresistance (MR) behavior, lower noise levels, negligible hysteresis and low cost of preparation. Especially, the granular alloys get importance in such areas of applications where magnitude of MR and sensitivity are not primary requirement.

It is known that the crystallographic structure produced by electrodeposition may or may not result into identical as produced by ordinary metallurgical process [24,25]. Generally, when metals are codeposited at lower polarization values, it gives rise to solid solution or supersaturated solid solution phases [24] and allows grain growth to occur. And this can happen even for binary immiscible metal pairs. The codeposition at high polarization, on the other hand, results into a two-phase alloy even for systems capable of forming continuous series of solid solutions [24,26]. Apart from this, high overpotential leads to formation of a large number of nuclei and makes it suitable for adatoms to crystallize even at unfavorable sites which again help in the formation of heterogeneous structures [27]. Application of pulse electrodeposition along with higher polarization further supports this process by inhibiting the grain growth of individual nuclei. Moreover, the magnetic response of the granular phase can be tailored by improving the structure, morphology and distribution within the dispersed phase, which depends on the free energy of heterogeneous phases and separating interfaces. Pulse electrodeposition, being a high energetic process, would be a better alternative to overcome such free energy barrier and limits the grain size in the nanometer range than the conventional direct current (DC) technique. Thus, it is quite expected

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hereto about the formation of supersaturated two-phase Cu–Co structure under pulse electrodeposition. The details of the pulse deposition, deposits phase and crystal structure analysis were presented elsewhere [28]. Reports on magnetoresistance properties of Cu–Co alloys with Co-content higher than 35 at.% are also limited in the literature [29].

In the present study, we performed the magnetization and magnetoresistance measurements of all the electrodeposited Co–Cu alloys films in detail. The effect of current pulsing, additive agent and annealing on magnetization and magnetoresistance was investigated.

2. Experimental

Co–Cu alloy specimens were electrodeposited galvanostatically on Si(1 1 1)/Ti(50 nm)/Cu(50 nm) substrates using a two electrode system which can provide DC as well as square wave current pulses. A standard oscilloscope was used to measure the rectangular pulses supplied by pulse power supply. A Pt metal sheet was used as anode. The chemical composition of the bath was 0.15 M $CuSO_4$, 0.6 M $CoSO_4$, 0.4 M H_3BO_3 and 0.3 M sodium citrate. The pH was maintained at 6. Saccharine (0.1 g L^{-1}) was added as a grain refining additive agent. For magnetic and magnetoresistance measurements, the specimens were prepared at two different current densities 6 mA cm^{-2} and 8 mA cm^{-2} using pulse current (PC) and DC modes as given in Table 1. The corresponding compositions are $Cu_{62.5}Co_{37.5}$ and $Cu_{47}Co_{53}$, respectively. The typical thickness of the alloy films grown was ~300 nm. X-ray diffraction (XRD, 3003-TT, Seifert, Ahrensburg, Germany) of the CoCu thin films was carried out using Cu K_α-radiation to determine the grain size of as-deposited alloys keeping incident beam at grazing angle of 0.3° to the sample surface in the θ–2θ geometry with a scan a rate of 0.02°/s. The grain size was calculated from the line-broadening of the X-ray peak using Wagner and Aqua [30] method. Here, the Gaussian distribution of the diffracted peaks (1 1 1) and (2 2 2) was used for separating the grain size and microstrain contribution to the peak broadening.

Magnetization measurements with respect to the magnetic field and temperature were performed using SQUID magnetometer. Magnetoresistance (MR) measurements for all the samples were carried out at room temperature using four probe method with applied magnetic field in the range of −7.5 to +7.5 kOe. These measurements were performed with current-in-plane geometry using an electromagnet while keeping the magnetic field perpendicular to the direction of applied current (transverse mode). Magnetoresistance in this paper is defined as $MR = \Delta R/R = (R_H - R_{Max})/R_{Max}$, where R_H is the resistance measured in a magnetic field H and R_{Max} is maxima of resistance measured as function of field. MR measurements were also carried out on samples after annealing at 450 °C for 1 h in a vacuum of 5.5×10^{-5} mbar.

3. Results and discussion

3.1. Magnetization of CoCu alloy films

Magnetization (hysteresis) loops were obtained at room temperature for PC-1 as-deposited alloys under no-additive (NA) and with additive (WA) conditions up to a maximum field of 1.5 T as shown in Fig. 1. For comparison, hysteresis loops for annealed samples are also shown in Fig. 1. The measured coercivity of PC-1-NA sample is 10 Oe, however; it exhibits saturation in magnetization at highest applied magnetic field. A plot of dM/dT *vs. T* (applied magnetic field, H = 500 Oe) clearly indicates the presence of superparamagnetic (SPM) regions with the appearance of blocking temperature (T_B = 50 K) below room temperature (inset of *M–H* plot (Fig. 1)). Moreover, for as-deposited sample, a peak near 25 K

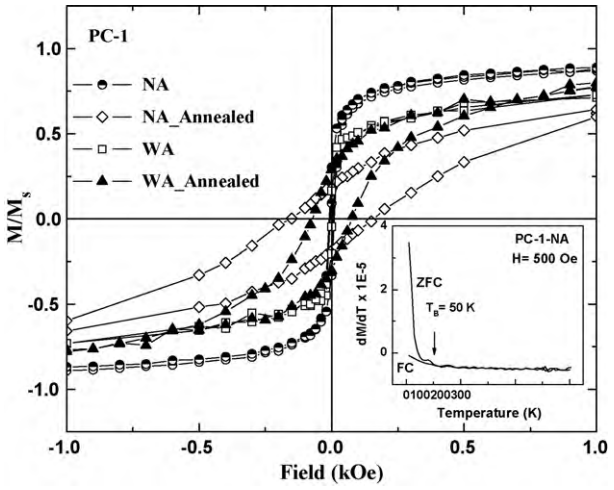

Fig. 1. *M–H* plot of PC-1 samples under as-deposited, in the presence of saccharine and post-annealed conditions. Inset shows *dM/dT vs. T* plot for PC-1-NA sample indicating clear bifurcation for FC and ZFC curves at 50 K (= T_B).

in the ZFC curve, suggests the presence of very fine particles of the SPM Co or Co-rich Co–Cu alloy phase. These might have precipitated in the alloy film with a wide distribution of size range. This kind of structural information is indeed supported by the previous X-ray diffraction pattern showing existence of both solid solution and phase separated CuCo alloy films [18].

In the presence of additive (designated as PC-1-WA), the coercivity (5.5 Oe) is seen to reduce with enhanced unsaturation in magnetization indicating refinement in magnetic grain size as evidenced from crystallite size data measured from XRD (Table 1). This also supports our previous microstructural observation by TEM [18]. It is to mention here that the crystallite size measured from X-ray peak broadening is upper bound to the grain size measured from TEM microstructure as reported in earlier investigations on nanocrystalline Ni–Cu alloys [26]. This could be due to complex contribution of microstrain, crystallite size and other defects to the X-ray peak broadening. However, the calculated data provide a trend of grain size change due to additive agent and electrolysis conditions. It is seen to follow approximately in the magnetic grain size too, indirectly evident from the coercive field values. It is also true for other PC and DC plated alloys as will be seen later in this section.

Therefore, the resulting magnetic structure of PC-1 can be approximated as numerous Co-grains within SPM regions with a very few ferromagnetic (FM) regions distributed over the Cu-matrix under no-additive conditions. In the presence of saccharine, FM grain growth suppresses and results in more SPM grains.

Post annealing, a marked increase in coercivity (H_c = 151 Oe) is noticed for PC-1-NA sample. Certainly, this is due to the domain growth of ferromagnetic Co-regions via coalescence of isolated SPM granules and also contributions from phase separation of

Table 1
Selected PC and DC plated samples chosen for magnetic measurements, their crystallite size data under as-deposited condition and measured coercivity data including annealed samples.

Sample	Alloy composition	Crystallite size (nm)		Coercivity, H_c (Oe)			
		NA[a]	WA[b]	NA[a]	WA[b]	NA-annealed	WA-annealed
PC-1	$Cu_{62.5}Co_{37.5}$	56.4	36.3	10	5.5	151	76
PC-2	$Cu_{47}Co_{53}$	44.2	36.4	13	9	93	32
DC-1	$Cu_{62.5}Co_{37.5}$	61.1	33.5	14	6	–	104
DC-2	$Cu_{47}Co_{53}$	41.3	31.5	12	–	70	–

[a] NA, no-additive.
[b] WA, with additive.

Cu–Co solid solution phases [25]. However, for sample PC-1-WA, the extent of increase in coercivity, H_c, 76 Oe was not significant as compared to no-additive condition (151 Oe). It supports the magnetization results about the presence of finer grain size second phase Co-magnetic particles in PC-1-WA as compared to PC-1-NA. It is known that high temperature favors the diffusion process and hence phase separation in Co–Cu alloys [25]. However, the finer distribution of Co-granules within the copper matrix needs more time to coalesce each other resulting into a larger cluster formation.

A close look into the *M–H* curve further reveals that the order of M_r/M_s, H_c and *M–H* saturation trend is:

(a) Order of M_r/M_s: PC-1-NA > PC-1-NA-Anneled > PC-1-WA-annelaed > PC-1-WA
(b) Order of H_c: PC-1-NA-annealed > PC-1-WA-annelaed > PC-1-NA > PC-1-WA
(c) Magnetization saturation trend: PC-1-NA > PC-1-WA > PC-1-WA-annelaed > PC-1-NA-annealed

The other PC and DC samples follow the same order as can be seen from the respective figures latter. A detailed analysis of these orders can result into a detailed magnetic structural information for pulse and DC deposited films either deposited in the presence or absence of saccharine followed by their modifications after annealing. High M_r/M_s ratio, highest low field saturation trend and low H_c value for PC-1-NA sample compared to others, suggests that the film consists of large numbers of small FM grains with a narrow size range and very small coercivity giving rise to high remanence. The other reason could be due to shape effect of the locally formed FM regions in the alloy matrix. These FM grains are distributed in SPM dominated matrices as evident from FC-ZFC measurement. Upon annealing, the kinetic driven Co–Cu solid-solution phase formed electrolytically, starts separating from each other and results into two-phase structure. Secondly, the already phase separated Co-grains begin to enhance their size at the expanse of smaller FM and SPM grains via diffusion process. But this process leaves behind a large fraction of isolated SPM regions throughout the matrix which cannot come close each other. It leads to magnetic unsaturation even at highest applied field of 1.5 T in *M–H* measurement. However, the overall magnetization of the sample reduces and allows better spin alignment with large coercivity. Overall, the magnetic structure behaves like a ferromagnet with respect to its spin alignment.

In the presence of additive, a further refinement in grain size takes place with the formation of more SPM grains in PC-1-WA films. As a consequence, the coercivity reduces along with enhanced unsaturation in magnetization of PC-1-WA as compared to PC-1-NA alloy film. Upon annealing, the Co-phase separates, but the extent is not as much as the case for no-additive structure because of finer grain size. And it shows higher coercivity in comparison to as-deposited films. To form a similar grain structure like PC-1-NA-annealed sample, it needs higher aging period.

Fig. 2 shows the *M–H* hysteresis curves for samples deposited under DC condition (DC-1). We note that the alloy composition is identical to PC-1 sample. Similar to previous sample, both remanence magnetization and coercivity (H_c = 14 Oe) have non-zero values. This again signifies the presence of a mixture of SPM and FM Co granules within the film matrix. The measured coercive field for this sample is too negligible, but higher in comparison to PC-1-NA alloy. So, the size of the FM Co-clusters was comparatively larger in case of DC-1-NA as compared to PC-1-NA sample. This is in agreement with previous microstructural investigations [18]. The trend of coercivity and magnetization change under additive and annealing conditions is similar to PC-1 sample.

With further increase in Co-content within the copper matrix to 53 at.% in the sample PC-2-NA, the coercive field is found to increase

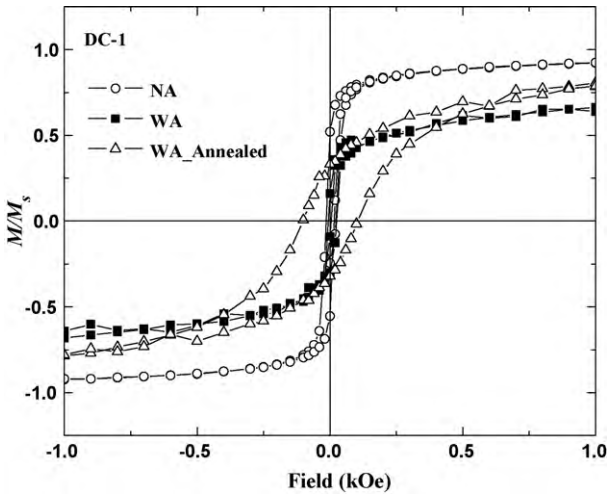

Fig. 2. *M–H* plot of DC-1 samples under as-deposited, in the presence of saccharine and post-annealed conditions.

slightly (13 Oe) in comparison to PC-1-NA sample (Fig. 3). A similar trend of coercivity change is observed in case of PC-2-WA sample as can be seen in Table 1. We note that the unsaturation trend in *M–H* behavior still exists even at highest applied magnetic field of 1.5 T. This indicates for the presence of SPM Co-granules within the copper matrix in a scattered manner even at this high concentration of cobalt. Therefore, it can be stated that the pulse electrodeposition being a higher energetic process helps better in dispersing the second phase Co-particles within Cu-matrix with enhanced heterogeneity. However, upon annealing at 450 °C for 1 h, a drastic change is reflected in the *M–H* curve with the appearance of large hysteresis and increased coercivity (93 Oe). For annealed no-additive and with additive PC-2 samples, the H_c values are 92 Oe and 32 Oe, respectively. We note that these values are smaller than PC-1 annealed samples (151 Oe and 76 Oe, respectively) even though PC-2 has higher Co-content. It signifies that higher pulse current density and hence higher polarization led to enhance nucleation and heterogeneity, which reflects in the magnetic behavior. To investigate the microstructural details further, magnetization was recorded under zero-field cooled (ZFC) and field cooled (FC) conditions (inset of Fig. 3). The ZFC curve shows a typical ferromagnetic behavior. This

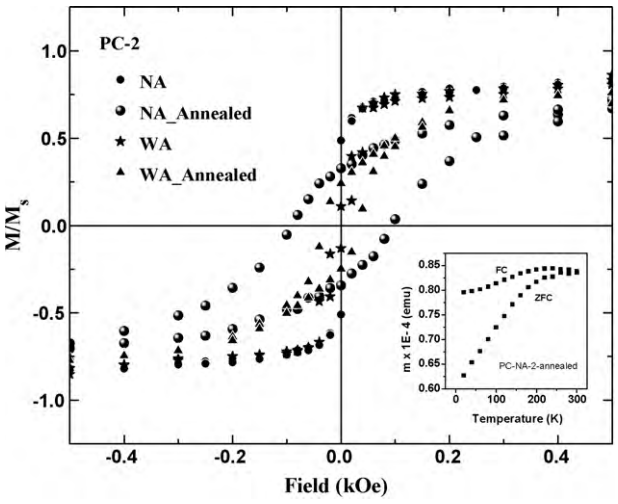

Fig. 3. *M–H* plot of PC-2 samples under as-deposited, in the presence of saccharine and post-annealed conditions. Inset shows *M–T* plot for annealed PC-2-NA sample with shifting of T_B near room temperature or above, a clear feature for FM-dominated structures.

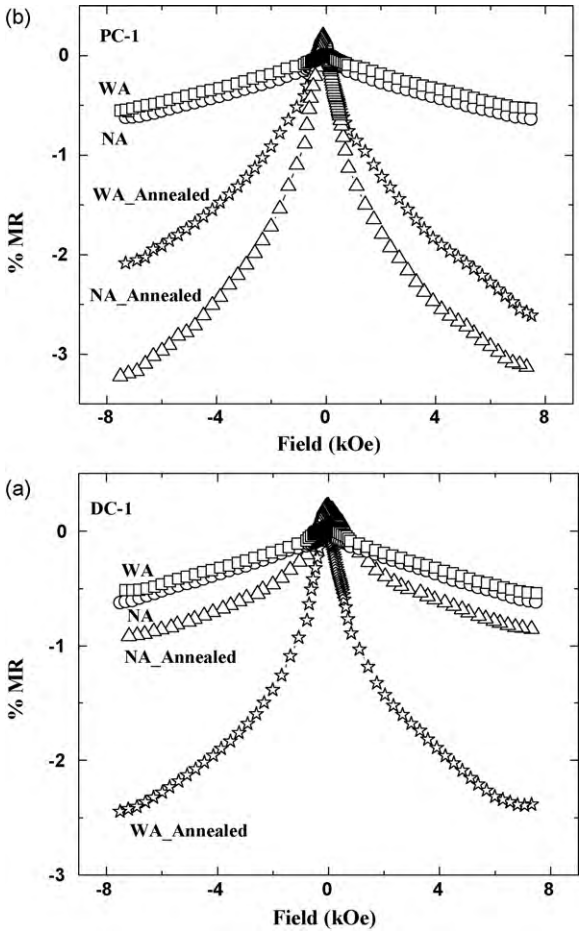

Fig. 4. MR curves for (a) PC-1 and (b) DC-1 samples.

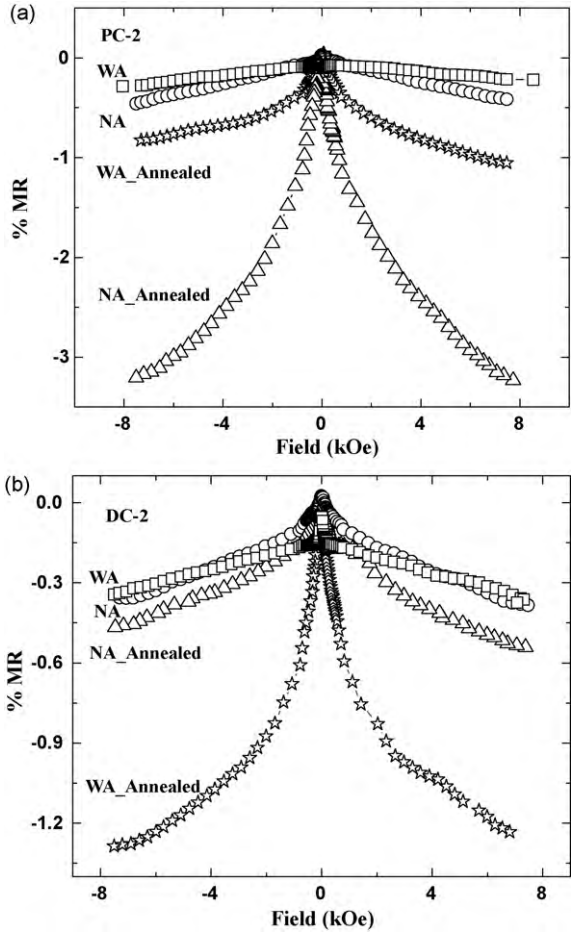

Fig. 5. MR curves for (a) PC-2 and (b) DC-2 samples.

indicates the existence of large ferromagnetic particles having a blocking temperature above room temperature arising from the phase separation of Co and Cu.

The coercivity of sample DC-2 was also found to increase after annealing as mentioned in Table 1 because of larger magnetic domain formation due to grain growth.

3.2. Magnetoresistance (MR) of CoCu alloy films

Figs. 4 and 5 show the magnetoresistance results for PC and DC samples under as-deposited and annealed conditions. All the samples showed unsaturated hyperbolic MR behavior up to the maximum field of ±7.5 kOe, indicating existence of SPM Co granules. For as-deposited samples PC-1 and DC-1, the obtained MR values are close to 0.5%, which is in agreement with previous observation by Péter et al. [29]. This is a typical feature of anisotropic magnetoresistance (AMR) of bulk ferromagnetic alloys (LMR component is not shown here). Upon annealing at 450 °C for 1 h, the MR percentage was found to increase several times with enhanced unsaturation. This is a typical feature of giant magnetoresistance (GMR) [2] because of separation of cobalt granules via Cu-phase within the spin diffusion length. After annealing, we note that in case of PC, the samples deposited without any additive results into maximum MR unlike DC samples which in the presence of additive give rise to a maximum MR. A maximum MR was obtained for PC-1-NA was 3.2% whereas DC-1-NA showed 2.5%. This is due to lower heterogeneity in DC-1-NA sample, which reflects in higher coercivity value (14 Oe) as compared to PC-1-NA (10 Oe). Upon annealing, the extent of thermal driven phase separation was also naturally lower which directly reduces the probability of formation of required magnetic spin structure arrangement for GMR phenomena to occur following Rutherman–Kittel–Kasuya–Yosida (RKKY) [31] interlayer exchange coupling. This means two FM grains separated via a Cu-spacer layer within the spin-diffusion length locally (Co/Cu/Co/Cu regions) within the Cu–Co matrix is not able to evolve smoothly like in PC plated alloys. Actually, it depends upon the Cu-layer thickness whether strong antiferromagnetic or ferromagnetic exchange coupling occurs between two neighboring isolated Co-regions. Upon annealing, two phases separate locally and forms a FM-NM (non-magnetic)-FM regions easily by diffusion allowing spin-dependent exchange interaction to occur for GMR while carrying the electrical current.

Whereas in case of PC-1-WA sample because of comparatively finer grain size, the given thermal treatment (450 °C for 1 h) might not be sufficient to coalesce the isolated SPM Co-grains to form sufficiently large FM-regions giving rise to equal exchange interaction as much in PC-1-NA samples. Therefore, the resulting MR is lower than no-additive condition. The other reason could be due to the formation of suitable Cu-spacer layer thickness between FM/SPM Co-regions resulting into overall high interlayer exchange coupling obeying RKKY-behavior.

It is interesting to note that the alloy of composition $Cu_{47}Co_{53}$ also shows ~3.2% GMR after annealing. Therefore, it is needless to mention here that the pulse plating is an efficient technique to make a Co-rich alloy into an SPM dominated structure with FM regions separated via Cu-boundary wall.

4. Conclusions

The present magnetic and magnetoresistance studies indirectly conclude that pulse plating is a better tool in segregating the Co-grains within the electrodeposited Co–Cu alloys containing even very high cobalt fractions. The structural heterogeneity further enhances due to the presence of brightening agent like saccharine in the electrolyte. Annealing at high temperature helps in transition from SPM to FM Co-regions locally separated via Cu spacers due to phase separation. Additive agent has significant effect on phase separation of DC deposited alloys. A maximum 3.2% GMR at room temperature with coercivity of 32 Oe was obtained for annealed pulse plated $Cu_{62.5}Co_{37.5}$ alloy and can be a potential candidate for low field sensor applications.

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