Electrodeposition of Cobalt Platinum Alloys Micromagnets

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Cobalt Platinum alloys are intensively investigated for application in magnetic micro- and nanodevices. The magnetic properties of layers of Cobalt Platinum alloys are mainly related to their microstructure and crystallographic preferred orientation (P.O.). Electrodeposition of relatively thick layers of Cobalt Platinum alloys was carried out from alkaline citrate and glycine solutions. Tungsten and Zinc were added to improve and control the properties of the deposited layers. Deposits with strong *hcp* [00.1] P.O. have perpendicular magnetic anisotropy, those with mixed crystallographic orientations are magnetically isotropic, and those with [11.0] P.O. have parallel magnetic anisotropy. The effect of Cobalt and Platinum interaction on the ferromagnetic behaviour of the electrodeposited alloys was investigated by means of X-ray Photoelectron Spectroscopy.

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Introduction

The production of micro and nanostructured materials is the demanding challenge for the future smaller, faster and less expensive electronic devices. For instance, the integration of ferromagnetic materials in MEMS can lead to outstanding high-force microactuators and low-power microsensors¹. In recent years great interest has been devoted to electrodeposited Cobalt Platinum alloys with perpendicular anisotropy, which makes them a very interesting material for perpendicular high density magnetic recording media. At the present, magnetic layers for high density magnetic recording are produced by sputtering while Cobalt Platinum alloys can be also produced by electrodeposition, which is a low-cost, versatile and very practical technique. The electrodeposition process can also overcome some limits of metallurgical and vacuum processes in MEMS integration, such as the requirement of high-temperature post-processing annealing.

The magnetic properties of electrodeposited alloys depend on their composition and crystallographic structure, which can be controlled by changing the electrochemical parameters, current density and temperature, and the electrolyte composition, mainly the pH. Cavallotti et al.² showed that Co electrocrystallisation can occur through three main growth modes depending on electrolyte composition and pH: outgrowth or perpendicular growth, lateral growth and cluster growth. The same authors³ showed the dependence of the magnetic properties on the crystallographic structure in Cobalt Platinum alloys. CoPtW(P) and CoPtZn(P) alloys with perpendicular growth have shown perpendicular magnetic anisotropy, *i.e.* their perpendicular coercivity $H_c(\perp)$ is higher than the parallel one $H_c(//)$; a lateral crystallographic growth gives CoPt alloys with parallel magnetic anisotropy, while alloys with weak perpendicular crystallographic preferred orientation P.O. or P.O.s with both perpendicular and parallel components are magnetically isotropic. They also show the effect of some electrochemical parameters on the crystallographic structure and composition of CoPtZn(P) and CoPtW(P) alloys. CoPt(P) alloys with Pt>20at% show very strong perpendicular anisotropy and high magnetic coercivity in perpendicular direction (H_c (\perp)=320 kA m¹) even though the magnetic properties drop as the layer thickness is higher than 1 μ m. By adding a third alloying element it is possible to completely change the magnetic properties of the material. CoPtW(P) and CoPtZn(P) alloys can show very good perpendicular anisotropy even at high thickness (10 µm). In CoPtW(P) alloys the Platinum content is lower compared to CoPt(P) alloys of similar magnetic behaviour, thus their cost can be theoretically decreased.

The aim of the present study is to contribute to a better understanding of the properties of electrodeposited CoPt(P) magnetic alloys. In particular the relation between the crystallographic structure and the magnetic properties is discussed and the results of X-ray Photoelectron Spectroscopy analysis of CoPt(P) alloys are presented.

Experimental

The plating solutions were prepared from chemicals of analytical grade and doubly distilled water. The composition of the electrolytes is reported in Table 1.

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Chemicals	CoPt(P)	CoPtW(P)	CoPtZn(P)
$Co(NH_2SO_3)_2$	0.1M	0.1M	0.1M
$Pt(NH_3)_2(NO_2)_2$	0.01M	0.01M	0.01M
$(NH_4)_2C_6H_6O_7$	0.1M	0.1M	0.1M
NH ₂ CH ₂ COOH	0.1M	0.1M	0.1M
Na ₂ WO ₄ ·2H ₂ O	-	0.27M	-
$Zn(NH_2SO_3)_2$	-	-	0.005M
рН	8	8	8

 Table 1. Composition of the electrolytes for CoPt(P), CoPtW(P)

 and CoPtZn(P) alloys electrodeposition.

Temperature was in the range of 40 to 80°C. The current density was in the range 5 to 60 mA cm⁻². Electrolyte pH was adjusted by addition of either sodium hydroxide or sulphamic acid. Electrodeposition experiments were carried out by means of a power supply (AMEL 550) in constant current density mode. Substrates (brass, copper sheets or silicon wafers coated with gold or copper) were degreased with acetone and activated by means of a dilute solution of sulphamic acid and finally thoroughly rinsed with doubly distilled water. Phase structure and texture of deposited films were determined by X-ray diffractometry (XRD) with CuK α radiation and a powder goniometer (Philips PW1830). The composition was measured by EDS analysis; thickness and morphology were assessed by laser profilometry (UBM Microfocus) and SEM (Cambridge Stereoscan 360), respectively. Room temperature hysteresis cycles were determined by VSM (Vibrating Sample Magnetometer) MOKE (Magneto-Optical Kerr Effect) techniques in magnetic field both perpendicular and parallel to the substrate. The XPS measurements were carried out on a PHI 5600 ci ESCA system. Operating conditions are reported in Table 2.

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T arameters	
Al Ka excitation	$h \pm = 1486.6 \text{ eV}$
Pass energy	11.75 eV
Time/step	100 ms
eV/step	0.05 eV

The calculation of the alloy XPS spectra was done by using the experimental XPS spectra of Cobalt foil 99.99% (Alfa Aesar), Platinum foil 99.99% (Alfa Aesar), bulk Cobalt (II) oxide, Tungsten and Zinc. The spectra were acquired after a sputtering of about 1000 Å (sputtered area 4x4 mm, emission 15 mA, beam voltage 4 keV) to remove contaminated surface layers. The sputtering rate was 3.7 nm min⁻¹ referred to standard SiO₂ on Si. The binding energy of CoP photopeaks was referred to the C 1s peak at 284.5 eV. PHI software was used to obtain peak areas and to calculate atomic concentrations. A 45° take-off angle was used for analyses.

Results and Discussion

The main parameters derived from hysteresis cycles, recorded both parallel (//) and perpendicular (\perp) to the substrates, are the coercivity H_c (kA m⁻¹), the saturation magnetisation J_s (T), the remanence J_r (T) and the squareness J_r/J_s .

The magnetic properties of Cobalt Platinum alloys depend on the composition and the crystallographic structure of the layers. The alloys electrodeposited from electrolyte of Table 1 are Co-rich and have hexagonal close-packed (*hcp*) crystallographic structure with different preferred orientations (P.O.), depending on the operating conditions. Three main magnetic behaviours were observed: CoPtZn(P) and CoPtZn(P) samples with pronounced [00.1] P.O., i.e. with magnetic easy direction perpendicular to the substrate, have strong perpendicular magnetic anisotropy, being perpendicular coercivity (H_{c,⊥}) higher than the parallel one (H_{c, //}) (Figure 1-Figure 3).



Figure 1. Hysteresis cycle of the sample S1 (CoPtZn(P) alloy) measured by VSM.



Figure 2. Hysteresis cycle of the sample S4 (CoPtW(P) alloy) measured by VSM.



Figure 3. Hysteresis cycle of the sample S5 (CoPt(P) alloy) measured by MOKE magnetometer.

These samples growth with the characteristic columnar morphology displayed in Figure 4.



Figure 4. Typical cross-section morphology of Cobalt Platinum alloys with perpendicular magnetic anisotropy.

CoPtZn(P) samples with [00.2]+[11.2] reflections can be characterised either by low perpendicular anisotropy or by magnetic isotropy, being perpendicular and parallel anisotropy values very similar (not shown). Magnetic isotropy was shown also by CoPtZn(P) deposits characterised by [00.1] + [11.0] or [00.1] + [10.0] or [11.0] + [11.2] reflections (the latter probably corresponding to a [00.1] + [11.0] structure where (00.2) planes were not differentiated by XRD analysis). Finally, CoPtZn(P) films with pronounced [11.0] P.O., i.e. with magnetically easy direction parallel to the substrate, have parallel magnetic anisotropy (Figure 5-Figure 6).



Figure 5. Hysteresis cycle of the sample S2 (CoPtZn(P) alloy) measured by VSM.



Figure 6. Hysteresis cycle of the sample S3 (CoPtZn(P) alloy) measured by VSM.

Coercivity of CoPtZn(P) alloys is asymptotic for film thickness higher than about 2.5 μ m, as observed for CoPt films⁴. H_{c, //} decreases by increasing current density, as shown in Figure 7. Coercivity values decreased markedly at lower temperature.



Figure 7. Parallel coercivity H_{//} of CoPtZn(P) alloys as a function of the current density at 80°C.

The squareness of the hysteresis cycles is generally lower than 0.5. This observation is in agreement with calculated values of Quinn *et al.*⁵ and Chikazumi⁶, about 0.866 and 0.5 respectively for disordered *fcc* and *hcp* structures, and lower than 0.5 for a partly ordered *hcp* structure.

The theoretical XPS spectra of the alloys were calculated as weighted sum of the valence bands of the elements (Cobalt, Platinum, Tungsten and Zinc). The normalised experimental valence band of Cobalt is shown in Figure 8. The total area of the valence band is 3.77, the electronic configuration of the external shell of Cobalt is $3d^74s^2$ and the total number of electrons in the valence band is 9. Therefore the value of the area/electron ratio is 0.42.



Figure 8. Normalised experimental valence of Cobalt foil.

In Figure 9 the normalised experimental valence band for Platinum is displayed. The total area of the band is 5.51, and considering that the electronic configuration of the external shell for Platinum is $5d^96s^1$ and the total number of electrons is 10, thus the area/electron ratio is equal to 0.55.



Figure 9.Normalised experimental valence band of Platinum foil.

The electronic configuration of the valence shell of Zinc is $3d^{10}4s^2$, the total area of the normalised experimental valence band is 1.46 (Figure 10) and the area/electron value is 0.12.



Figure 10. Normalised experimental valence band of bulk Zinc.

Finally Tungsten has the external shell $5d^46s^2$; the total area of the valence band is 3.595, therefore the area/electron ratio is 0.6 (Figure 11).



Figure 11. Normalised experimental valence band of bulk Tungsten.

The EDS atomic compositions of the alloys were divided by the value of the area/electron ratio calculated as described before. The weights used to calculate the theoretical spectra were obtained by normalising the resulting values by the sum of all the contributes (Table 3).

Sample	Metal	Metal content (at%)	Area/electron	Weights	Normalised weights
S 1	Со	89.4	0.42	212.9	0.84
	Pt	7.3	0.55	13.3	0.05
	Zn	3.3	0.12	27.5	0.11
Total	100.0		253.6	1.00	
S2 Co	Со	87.5	0.42	208.3	0.84
	Pt	9.5	0.55	17.3	0.07
	Zn	2.8	0.12	23.2	0.09
	Total	100.0		248.8	1.00
S3 Co Pt	Со	81.6	0.42	194.3	0.72
	Pt	11.8	0.55	21.4	0.08
	Zn	6.6	0.12	55.1	0.20
	Total	100.0		270.8	1.00
S4	Со	87.0	0.42	207.1	0.90
	Pt	10.0	0.55	18.2	0.08
	W	3.0	0.12	5.0	0.02
Total	100.0		230.3	1.00	
S5 Co Pt W Total	Со	87.0	0.42	207.1	0.90
	Pt	10.0	0.55	18.2	0.08
	W	3.0	0.12	5.0	0.02
	Total	100.0		230.3	1.00

Table 3. Elemental atomic composition and weights for CoPt(P), CoPtZn(P) and CoPtW(P) alloys.

A comparison between the experimental and the calculated XPS spectra pointed out a difference in the Fermi energy of about 0.6 eV, which was partially corrected by shifting the experimental curve. The shift moved the experimental spectra toward higher energy values for S1, S2 and S3 (CoPtZn(P) alloys) and S4 (CoPtW(P) alloy) while toward lower energy values

for S5 (CoPt(P) alloy). In Figure 12-Figure 16 the calculated and experimental XPS spectra of CoPt(P), CoPtZn(P) and CoPtW(P) alloys are compared.



Figure 12. S1: a- calculated; b-experimental; c: experimental-calculated.



Figure 13. S2: a- calculated; b-experimental; c: experimental-calculated.



Figure 14. S3: a- calculated; b-experimental; c: experimental-calculated.



Figure 15. S4: a- calculated; b-experimental; c: experimental-calculated.



Figure 16. S5: a- calculated; b-experimental; c: experimental-calculated.

By calculating the difference between the experimental and the calculated XPS spectra a band in the range 1-10 eV is obtained. This band might be caused by a charge transfer between Cobalt and Platinum. The intensity of this peak is linearly dependent on the Pt/(Pt+Co) atomic ratio in the layers and not affected by the Zinc and Tungsten contents (Figure 17). The peak area increases with increasing the Platinum content (Table 4) and might be related also to the presence of Cobalt oxides, whose contribution was not considered in the calculation of the theoretical spectra of the alloys. Tungsten might be present not only as an alloying element but also as oxidised salts at grain boundaries. Similarly, Zinc is likely to be present in the deposit also as oxidised compounds (oxides or hydroxides) precipitated at grain boundaries. On the other hand, Phosphorus is not an alloying element but probably precipitates at grain boundaries in the form of phosphates or phosphides compounds.



Figure 17. Normalised peak intensity as a function of the relative Pt content in the alloys.

Pt/(Co + Pt)	Band Area (eV)
0.055	0.343
0.075	0.993
0.098	1.176
0.103	1.437
0.126	2.675

Table 4. Relative Platinum contents and areas below curves c (Figs.12-16).

The comparison between Pt 4f photopeaks of S5 sample and Pt foil 99.99% suggests that in the alloy a possible hybridization between Cobalt and Platinum 'd' orbitals, with stabilization of the 4f Pt orbitals, can occur (Figure 18). In fact the Pt $4f_{7/2}$ peak shifted from 71.2 eV in the Platinum foil 99.99% to 71.8 eV in the sample S5. On the other hand, no shift of the Co $2p_{3/2}$ photopeaks of S5 sample with respect to Co foil 99.99% was observed (maximum at 778.3 eV, Figure 19).



Figure 18. Comparison between normalised intensity of Pt 4f photopeaks for S5 sample (red line) and Pt foil 99.99% (purple line).



Figure 19. Comparison between normalised intensity of Co 2p 3/2 photopeaks for S5 sample (red line) and Co foil 99.95% (blu line).

Conclusions

The present study is devoted to a better understanding of the magnetic properties of CoPt(P), CoPtZn(P) and CoPtW(P) electrodeposited alloys. These alloys show different magnetic behaviours in relation to the preferred orientation of their crystallographic structure. Perpendicular magnetic anisotropy was shown by CoPt(P) alloys with strong [00.1] P.O., while parallel magnetic anisotropy was observed in CoPtZn(P) alloys with P.O. parallel to the substrate. A further investigation of the properties of these alloys was performed by means of X-ray Photoelectron Spectroscopy in the valence band region. By comparing the experimental with the calculated spectra an energy difference was observed. The corresponding band can be due to a charge-transfer interaction between Cobalt and Platinum. This observation is consistent with the valence band shift of Platinum 4f electrons toward higher energies. Moreover, both the peak intensity and the peak area of the band are proportional to the relative Platinum content in the alloys, confirming the strong interaction of Platinum with Cobalt and its role in determining the anisotropy field of the alloy.

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