Electrodeposition of New Magnetic Materials

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Magnetic materials are widely used in the different fields of technical applications e.g. sensors and actuators. With the ever accelerating process of the miniaturization of microelectronic, micromechanical and magnetic components the application of new technologies for the synthesis of such magnetic materials is necessary. For the preparation of magnetic materials in thin layers (up to 10 μm) mostly vacuum processes like PVD, CVD and MBE are used whereas for structures in dimensions over 600 μm sintering and casting techniques can be applied. The technological gap between these two dimensions can be filled by electrochemical deposition as a low cost process with high potentialities for the application especially for the preparation of micro sized magnetic components. A successful introduction of electrochemical techniques into production processes is only possible with a good knowledge about the correlation between the process parameters and the properties of the deposited materials. In the presentation an overview of electrodeposition of PtCoW alloys is given.

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Introduction

Magnetic materials find application in many different technical fields. Especially for the fabrication of microelectronic and micromechanical devices the normally used processes like powder metallurgy or casting cannot be used, because the magnetic materials have to be introduced as system parts and it is impossible to decrease the dimensions of the presently most used rare earth permanent magnets. In the field of microelectronics, in most cases vacuum deposition processes e.g. PVD, CVD and MBE are used but the possible layer thickness is limited to some micrometers. In the last years electrochemical deposition is becoming more and more considered as an alternative for the fabrication of magnetic materials, to fill the gap in dimensions between vacuum and metallurgy processes [1-8]. With these techniques a low cost process is available especially for the fabrication of microsystems which can have a complex shape and a high aspect ratio.

For the application of electrochemical processes and in order to improve the performance of these materials a better understanding of the mechanism of the deposition process and of the influence of the different process parameters onto the layer properties is needed.

In the following the electrodeposition of permanent magnetic materials of cobalt-platinum-tungsten-alloys is described.

Experimental

Electrolyte

The composition of the electrolyte used for the electrodeposition of the PtCoW-alloy is given in the following table 1:

0.1 M Cobaltsulphamate	$Co(SO_3NH_2)_2$
0.01 M Platinum-p-salt	$Pt(NH_3)_2(NO_2)_2$
0.1 M Ammoniumcitrate	$(NH_4)_2C_6H_6O_7$
0.1 M Glycine	NH_2CH_2COOH
0.05 M Sodiumhypophosphite	$NaPH_2O_2{*}H_2O$
0.2 M Sodiumtungstate	$Na_2WO_4{*}2H_2O$

table 1: composition of the electrolyte

The standard deposition conditions of the electrolyte are described in the following table 2:

temperature	60 °C
pH-value	8
current density const. current	10 mA/cm^2
current density pulse cond.	10–400 mA/ cm^2

table 2: deposition conditions

Substrate materials

The deposition was carried out onto copper substrates. To improve the accuracy of the analysis of the composition of the cobalt-platinum-tungsten-alloys also aluminum and steel substrates were used and removed before the analysis.

Results and discussions

Composition of the layers

The composition of the layers was investigated by EDX and ICP analysis. The homogeneity of the layer in dependence of the layer thickness were analyzed by SEM and GDOS.

The integral values of the composition of the layers are varying in a wide range. For cobalt the concentrations are in the range between 53 and 82 w%, for platinum between 10 and 34 w% and for tungsten between 4 and 22 w%. This strong variation of the composition is caused by the layering of the alloys (see figure 7). For the electrodeposition of CoPtW-alloys a codeposition of high amounts of hydrogen is typical. The hydrogen is bound strongly in the alloys. To remove the hydrogen completely from the alloys a heat treatment of 24 hours at 500°C is necessary. The average of the hydrogen content of different samples in dependence of the heat treatment is shown in figure 1.

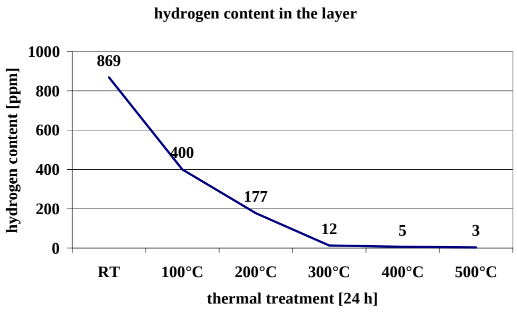

Fig. 1: hydrogen content in the layers

In addition to the high hydrogen content also a very high amount of oxygen and nitrogen is incorporated into the layers. The oxygen content is in the range between 0,85 and 3,03 w% and the nitrogen concentration is between 0,10 and 0,16 w%. The high concentration of oxygen is related to the concentration of tungsten and so an incorporation of tungsten oxide into the layers can be assumed.

After the thermal treatment a homogeneous distribution of the different alloy components can be determined by EDX and GDOS analyses.

Critical layer thickness for crack formation

CoPtW layers of different thickness were deposited at standard conditions. Using Scanning Electron Microscope, the surface of the layers was evaluated in view of cracks. Afterwards, the critical layer thickness for the formation of cracks was determined by cross-sectional analysis.

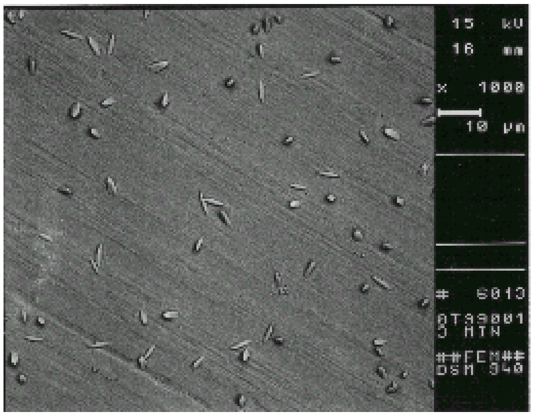

figure 2: CoPtW layer without cracks

In the SEM pictures in figure 2 and 3 the surface of CoPtW layers before and after crack formation is shown.

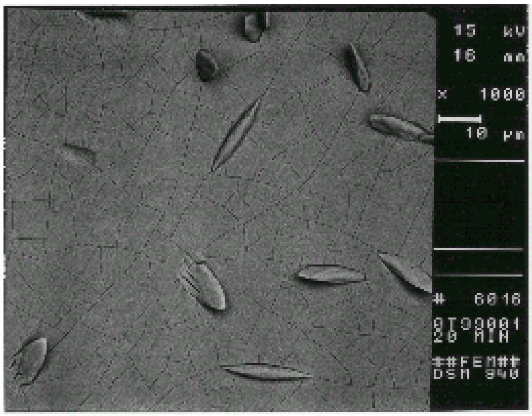

figure 3: CoPtW layer after crack formation

A visible crack formation is starting at a deposition time between 3 and 5 minutes. This corresponds to a layer thickness of approximately 100 nm. With deposition time, the crack frequency increases and the cracks become more and more visible. Further more, in most sample areas, particles are embedded in the deposit. EDX-spectra were recorded from the surface area and from the particle area and compared. From this it can be seen that the embedded particles show a much higher W-content than the CoPtW layer; oxygen was also detected.

The electrodeposition was carried out directly after a filtration procedure; therefore the precipitation containing tungsten and oxygen was built during electrodeposition and is not coming from a contamination of the electrolyte.

In situ measurement of internal stresses of CoPtW layers

For the application of CoPtW layers a reduction in the crack formation is necessary. As the cracks are built due to internal stresses of the layers, stresses have to be reduced. The in situ measurement of stress using the MSM 200 can be applied to investigate the influence of the different process parameters onto the internal stresses of the layers. The MSM 200 measurement system is based on the following principle [9]. A one side isolated metal stripe is used as substrate for the deposition. Caused by the tensile or compressive stress formed during deposition the metal stripe tends to deformation. The metal stripe is maintained in its initial position during electrodeposition. The necessary force is measured by means of a detecting element. This force can be used to calculate the internal stress of the layer. The sensor system of the MSM 200 shows figure 4.

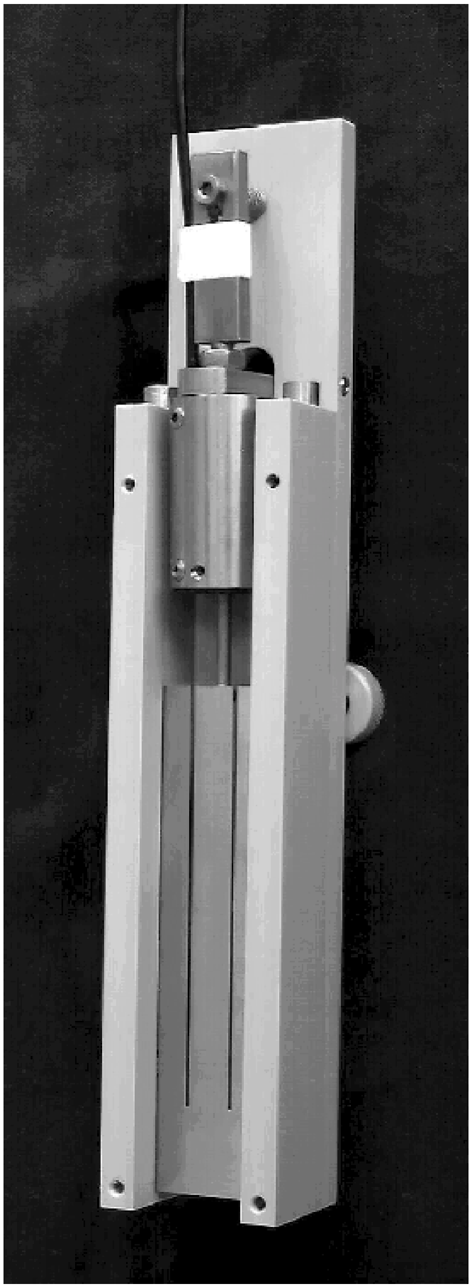

figure 4: sensor of the MSM 200

By the application of pulse current or current breaks the internal stress of the layers can be influenced. In figure 5 an example is shown, how the detecting force is changed in dependence of the current. In the shown sample the change in internal stresses is caused by the hydrogen release during the current break. The effect is increasing with the layer thickness because of the higher capacity of the layer to store hydrogen.

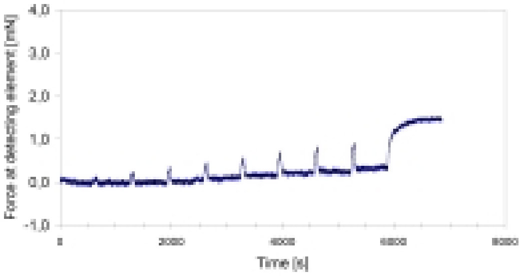

figure 5: measurement of internal stresses
[10 mA/cm^2 10 min, current break 1 min]

Electrodeposition in magnetic field

The effects on crystallographic structure and magnetic properties of CoPtW deposits applying a magnetic field during electrodeposition was studied. The plaiting cell was installed in between the pole shoes of a magnet. The position of the electrodes was either in perpendicular or in parallel direction to the magnetic field. Figure 6 shows the magnetic field distribution in horizontal and vertical direction starting from the center of the poles at a pole shoe distance of 45 mm.

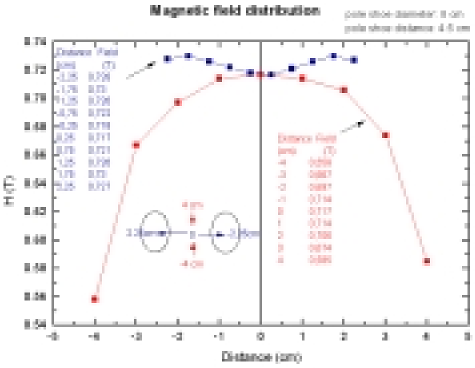

figure 6: distribution of magnetic field

The deposition in the magnetic field was carried out in a field of 0.3 and 0.6 T and a current density of 10 mA/cm^2. The influence of the field onto the structure of the layers is not understood completely at the moment. By switching the magnetic field in combination with the current on and off a layered structure can be achieved. During the phase of zero magnetic field and current an autocatalytic deposition is taking place, sometimes with a higher deposition rate in comparison to the phase with current. These layered structures can be deposited crack free. An example for such a layer is shown in figure 7.

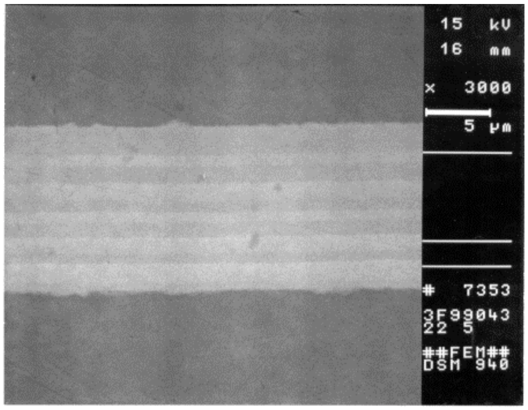

figure 7: deposition in magnetic field

An example that these layered structures are able to reduce the internal stress of the deposits and the tendency to the crack formation is shown in figure 8. The cracks are only formed in between non cracked layers.

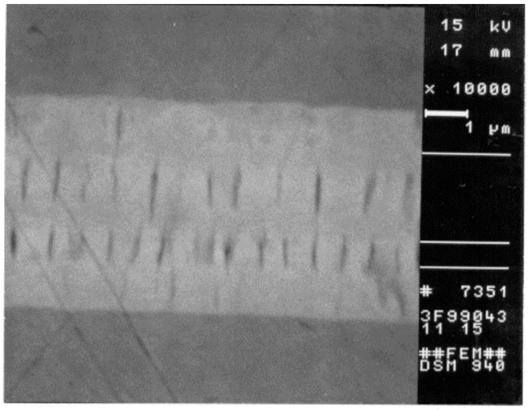

figure 8: alternating cracked/crack free layer

Magnetic properties of the layers

The magnetic properties of the samples were investigated using a Vibrating Sample Magnetometer (VSM). The hysteresis cycles were measured at room temperature applying the field in a direction parallel and perpendicular to the samples surface. The hysteresis cycle parameters of the layers are shown in table 3.

No	field parallel	field perpendicular
4	Hs>1A/m M(1A/m)= 0.770emu/mm^3 Mr=0.138emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=160 x 10^{-3} A/m	Hs>1A/m M(1A/m)=0.456 emu/mm^3 Mr=0.174emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc= 280 x 10^{-3} A/m
9	Hs>1A/m M(1A/m)=0.721 emu/mm^3 Mr=0.175emu/mm^3 (Mr-M(1))/M(1A/m)= Hc=191 x10^{-3} A/m	Hs>1A/m M(1A/m)=0.514 emu/mm^3 Mr=0.230emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=306 x10^{-3} A/m
19	Hs>1A/m M(1A/m)=0.728 emu/mm^3 Mr=0.222emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=213 x 10^{-3} A/m	Hs>1A/m M(1A/m)=0.506 emu/mm^3 Mr=0.120 emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=193 x 10^{-3} A/m
13	Hs>1A/m M(1A/m)=0.716 emu/mm^3 Mr=0.088emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=98 x 10^{-3} A/m	Hs>1A/m M(1A/m)=0.532 emu/mm^3 Mr=0.195emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=279 x 10^{-3} A/m
12	Hs>1A/m M(1A/m)= 0.895emu/mm^3 Mr=0.128emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=122 x 10^{-3} A/m	Hs>1A/m M(1A/m)=0.601 emu/mm^3 Mr=0.240emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=292 x 10^{-3} A/m
20	Hs>1A/m M(1A/m)=0.619 emu/mm^3 Mr=0.176emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=200 x 10^{-3} A/m	Hs>1A/m M(1A/m)=0.474 emu/mm^3 Mr=0.130emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=223 x 10^{-3} A/m
21	Hs>1A/m M(1A/m)=0.646 emu/mm^3 Mr=0.141emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=167 x 10^{-3} A/m	Hs>1A/m M(1A/m)=0.528 emu/mm^3 Mr=0.164emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=250 x 10^{-3} A/m
11	Hs>1A/m M(1A/m)=0.937 emu/mm^3 Mr=0.142emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=124 x 10^{-3} A/m	Hs>1A/m M(1A/m)=0.688 emu/mm^3 Mr=0.280emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=305 x 10^{-3} A/m
17	Hs>1A/m M(1A/m)=0.668 emu/mm^3 Mr=0.237emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=154 x 10^{-3} A/m	Hs>1A/m M(1A/m)=0.518 emu/mm^3 Mr=0.112emu/mm^3 (Mr-M(1))/M(1A/m)=- Hc=178 x 10^{-3} A/m

table 3: hysteresis cycle parameters (300 K)

The measured samples show magnetic anisotropy and are easily magnetised if the field is applied parallel to the sample surface. The coercive field is normally higher if the field is applied perpendicular to the sample surface. The coercivities are in the range of 0,1 to 0,2 A/m for the field applied parallel to the sample surface and are in the order of 0,18 to 0,30 A/m for the field applied perpendicular to the sample surface.

The highest coercivities can be measured for the samples with a platinum content of about 30 w% and a tungsten content less than 7 w%. A higher tungsten and lower platinum concentration reduces the coercivities. A clear influence of the magnetic field during the electrodeposition onto the magnetic properties cannot be found up to now. For a better understanding of the influence of the process parameters onto the structure of the layers and the magnetic properties further investigations will be carried out in future.

Conclusions

The presentation shows, that magnetic materials with a high coercivity can be synthesized by electrochemical techniques from aqueous solutions. Using these processes a deposition into microstructured systems is possible, allowing the implementation of permanent magnetic materials into microelectronic and micromechanic devices. This offers the possibility to easily build up sensors and actuators even with complex geometry. The application of such systems requires a better understanding of the correlation between the composition of the electrolyte and process parameters onto the structure and magnetic properties which is to be investigated in further research.

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References

[1] Fidler, J.; Bernardi, J.; Schrefl, T.
Scripta Metallurgica et Materialia, Vol. 33, N° 10/11, 1995, pp. 1781-1791

[2] Liakopoulos, T.; Zhang, W.; Ahn, C.
9th Annual International Workshop on MicroElectroMechanical Systems, San Diego, CA, USA, Feb 11-15, 1996

[3] Al-Omari, I.; Sellmyer, D.
The American Physical Society, Vol. 52, N°. 5, 1995, pp. 3441-3447

[4] Skomski, R.
Journal of Applied Physics, Vol. 76, N° 10, 1994, pp. 7059-7064

[5] Parhofer, S.; Wecker, J.; Kuhrt, C.; Gieres, G.
Transactions on Magnetics, Vo. 32, N° 5, 1996, pp. 4437-4439

[6] Jansen, H.
Physics Today, April 1995, pp. 50-55

[7] Popovic, R.; Flanagan, J.; Besse, P.
Sensors and Actuators, Vol. A56, 1996, pp. 39-55

[8] P. L. Cavallotti et al. Surface and Coating Technologies; 105, 232-239 (1998)

[9] A. R. Zielonka, H. G. Fauser, Proc. AESF SUR/FIN 99