



A MATERIAL FOR USE IN A MEMS DEVICE, A METHOD OF MAKING THE MATERIAL AND A MEMS DEVICE INCLUDING THE MATERIAL

FIELD OF THE INVENTION

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This invention relates to a material for use in a microelectromechanical system (MEMS) device, and to a MEMS device including such a material.

BACKGROUND TO THE INVENTION

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MEMS devices that include electro-magnetic microactuators usually require microstructures that have thick magnetisable films. Thick films are necessary for the associated magnetic fields set up therearound during operation to be of sufficient strength to operate the microactuators.

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An advantage of films of this kind is that material forming the film can be rapidly deposited by electroplating. However, a drawback of such thick films is that in-plane film stresses are intrinsically high. This can result in delamination and thus failure of films during heat treatment.

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An example of films of this kind is given in Singapore Patent Application No. 200403718-8, which was filed before but not yet published at the time of filing the present specification. That earlier application disclosed a composition of cobalt-nickel-rhenium-tungsten-phosphorous (Co-Ni-Re-W-P) that was formed by electrodeposition as hard magnetic films of high vertical magnetic anisotropy suitable for use in MEMS devices. A drawback, however, of such a composition is that its magnetic properties may deteriorate under exposure to high temperatures. For example, it has been observed that the vertical remnant magnetisation, M_r , and vertical coercivity, H_c , of the Co-Ni-Re-W-P composition deteriorate markedly upon annealing at a temperature of 200°C for 2 hours in ambient atmosphere.

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It is an object of at least certain embodiments this invention to address these problems of delamination and magnetic property deterioration.

SUMMARY OF THE INVENTION

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According to a first aspect of this invention, there is provided a multi-layered material for use in a microelectromechanical system (MEMS) device, the material including a plurality of layers of a magnetiseable material comprising cobalt, nickel, rhenium, tungsten and phosphorous (Co-Ni-Re-W-P), the or each adjacent pair of layers of Co-Ni-Re-W-P having
10 a respective layer of a non-magnetiseable, electrically-conductive material therebetween.

By providing a plurality of layers of Co-Ni-Re-W-P rather than a single, thick, layer, the layers of the material can each be thinner than the single, thick, layer. As a result, the multi-layered material does not tend to suffer from the poor mechanical properties and thermal
15 instability exhibited by the single layer. Instead, the resulting material is an improved material delivering high and stable out-of-plane magnetic properties. Thus the material is particularly suitable for the manufacture of MEMS devices and the low temperature annealing often involved therein.

20 According to a second aspect of this invention, there is provided a multi-layered material for use in a microelectromechanical system (MEMS) device, the material including a plurality of layers of a magnetiseable material comprising cobalt, platinum and phosphorous (Co-Pt-P), the or each adjacent pair of layers of Co-Pt-P having a respective layer of a non-magnetiseable, electrically-conductive material therebetween.

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Advantages that result from the first aspect of this invention are similarly advantages of the second aspect.

Preferably the multi-layered material includes at least five layers of the magnetiseable
30 material, each such layer being spaced from the or both adjacent layers of magnetiseable material by a respective layer of the non-magnetiseable, electrically-conductive material

therebetween. More preferably, there are between five and ten of layers of the magnetiseable material . For example, there may be five, six, seven, eight, nine or ten such layers.

- 5 In certain embodiments, the multi-layered material includes a base layer of the, or of another, non-magnetiseable, electrically-conductive material. The base layer may be a seed layer for binding the remainder of the multi-layered material to a substrate. A layer of chromium (Cr) may be provided between the base layer and the substrate. Thus, in these embodiments, each of the layers of magnetiseable material is a layer on a respective layer
10 of a non-magnetiseable, electrically-conductive material.

- Preferably, each of the layers of magnetiseable material has a thickness of at least $0.1\mu\text{m}$ and preferably less than $2\mu\text{m}$. Preferably, each of the layers of magnetiseable material has a thickness in the range of 0.5 to $1.5\mu\text{m}$. Preferably, each of the layers of magnetiseable
15 material has a thickness of approximately $1\mu\text{m}$.

- Preferably, each layer of the non-magnetiseable, electrically-conductive material that is disposed between a respective adjacent pair of the layers of magnetiseable material has a thickness of at least $0.1\mu\text{m}$ and preferably less than $0.5\mu\text{m}$. Each layer of the non-
20 magnetiseable, electrically-conductive material may have a thickness of approximately $1\mu\text{m}$.

- Preferably the base layer is of a lesser thickness, and may be approximately 200 nm thick. The Cr layer may have a thickness of approximately 20 nm .

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- The non-magnetiseable, electrically-conductive material may be, for example, gold (Au) or copper (Cu). Preferably, where the layers of magnetiseable material are of Co-Ni-Re-W-P, the non-magnetiseable, electrically-conductive material that is between adjacent pairs of layers of Co-Ni-Re-W-P is Cu. Preferably, where the layers of magnetiseable material are
30 of Co-Pt-P, the non-magnetiseable, electrically-conductive material that is between adjacent pairs of layers of Co-Pt-P is Au. Preferably the seed layer is of Au.

According to third aspect of this invention, there is provided a structure including the multi-layered material defined above, and further including the substrate.

5 Preferably the substrate is a glass substrate

According to a fourth aspect of this invention, there is provided a microelectromechanical system (MEMS) device including the structure defined above and/or the multi-layered material defined above.

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According to a fifth aspect of this invention, there is provided a multi-layered material for use in a microelectromechanical system (MEMS) device, the material including a plurality of layers of magnetiseable material, the or each adjacent pair of layers of magnetiseable material having a respective layer of a non-magnetiseable, electrically-conductive material
15 therebetween, wherein at least the layers of magnetiseable material are of a thickness in the range of 0.1 to 2 μm .

The magnetiseable material may include Co-Ni-Re-W-P. The magnetiseable material may include Co-Pt-P.

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Optional features of the aspects of the invention defined above may also be optional features of this fifth aspect of the invention.

According to a sixth aspect of this invention, there is provided a method of manufacturing a
25 multi-layered material for use in a microelectromechanical system (MEMS) device, the method including the steps of forming a plurality of layers of magnetiseable material, and a plurality of layers of non-magnetiseable, electrically-conductive material, the various layers formed one on top of another and alternately, with the or each adjacent pair of layers of magnetiseable material having a respective layer of non-magnetiseable, electrically-
30 conductive material formed therebetween.

The layers of magnetiseable material may be of, for example, Co-Ni-Re-W-P or Co-Pt-P. Preferably, all of the layers of magnetiseable material are of the same material.

5 The method may include the step of forming a first layer of the multi-layered material onto a substrate. The first layer is preferable a seed layer.

The method may include the step of forming the layers of magnetiseable material and/or the layers of non-magnetiseable, electrically-conductive material by electrolytic plating. Preferably the method includes the step of forming the layers of non-magnetiseable, electrically-conductive material by electroless plating. Preferably, the plating is conducted by placing the substrate into an electrochemical bath, and preferably the method includes steps in which the substrate is placed in such a bath. Preferably the bath is at a temperature below 30C, but may be at a temperature of between room temperature and 100C. Preferably the bath has a pH at or below 5.0.

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Features of the first to the fifth aspects of this invention may also be features of this sixth aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

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Specific embodiments of the present invention will now be described with reference to the accompanying drawings, in which:

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Figure 1 is a diagrammatic cross-sectional representation of a multi-layered material that embodies this invention;

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Figure 2 is a graph of the thickness of a deposited Co-Ni-Re-W-P layer of the material, against the duration of electrolytic plating operation bringing about the formation of that layer;

Figure 3 shows a hysteresis curve for a thick, single-layer, comparison material, the curve being a plot of the out-of-plane variation in absolute magnetisation of the material with variations in the strength of a magnetic field applied from an external source;

- 5 Figure 4 shows a hysteresis curve for a thin, single-layer, comparison material, the curve being a plot of the same variables as those shown in Figure 3;

Figure 5 shows a hysteresis curve for two multi-layered materials that embody this invention, the curve being a plot of the same variables as those shown in Figure 3 and

- 10 Figure 4;

Figure 6 is a reproduction of an image from a scanning electron microscope showing a cross-section through the thin single-layer comparison material;

- 15 Figure 7 is a reproduction of an image from a scanning electron microscope showing a cross-section through the thick single-layer comparison material.

Figure 8 is a reproduction of an image from a scanning electron microscope showing a cross-section through a first one of the multi-layered materials in which non-magnetisable
20 layers were deposited by electrolytic plating; and

Figure 9 is a reproduction of an image from a scanning electron microscope showing a cross-section through a second one of the multi-layered materials in which non-magnetisable layers were deposited by electroless plating.

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SPECIFIC DESCRIPTION OF CERTAIN EXEMPLARY EMBODIMENTS

This specific description begins with a description of a structure that embodies this invention and then describes a method, also embodying the invention, by which that
30 structure can be made.

Figure 1 is a schematic representation of a structure 10 that includes a multi-layered material 20. The structure 10 is for use in a MEMS device (not shown). The structure 10 includes a glass substrate 30 that has a thin layer of Cr 40 thereon. In this embodiment, the Cr layer 40 is approximately 20 nm thick. A thicker layer of Au 50 is formed on the Cr layer 40 and acts as a seed layer for the remainder of the multi-layered material 20. In this embodiment, the Au seed layer 50 is approximately 200 nm thick. The remainder of the multi-layered material 20 includes alternate layers of magnetiseable Co-Ni-Re-W-P 60 and of non-magnetiseable, but electrically conductive, Cu 70. The first layer on the Au seed layer 50 is a first Co-Ni-Re-W-P layer. In this embodiment, the multi-layered material includes six layers of Co-Ni-Re-W-P 60 with five layers of Cu 70. Thus, the layer of the multi-layered material furthestmost from the glass substrate 30 is a Co-Ni-Re-W-P layer 60.

In order to produce examples of the structure shown in Figure 1, the following method was performed.

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Aqueous bath solutions were prepared for the purposes of electroplating the layers of Co-Ni-Re-W-P 60 and of Cu 70. The bath for the Co-Ni-Re-W-P layers 60 was composed of 0.4 M B(OH)₃, 0.4 M NaCl, 0.05 M CoCl₂·6H₂O, 0.05 M NiCl₂·6H₂O, 0.007 M NH₄ReO₄, 0.001 M Na₂WO₄·2H₂O and 0.017 M NaH₂PO₃·2.5H₂O. The bath for the Cu layers 70 was made up of 0.315 M CuSO₄·5H₂O, 0.2 M Na₄P₂O₇·10H₂O and 1.6 M H₂SO₄. All solutions were prepared with pure deionised water. The pH of the bath solution for Co-Ni-Re-W-P layers 60 was adjusted to approximately 4.5 by using NaOH and H₂SO₄. The Cu bath solution for the non-magnetiseable layers of Cu was acidic with a pH of approximately 0.1.

Clean glass substrates, each substantially the same as that 30, were sputtered first with chromium (Cr) to a thickness of approximately 20 nm to form the Cr layer 40 thereon; followed by gold (Au) to a thickness of approximately 200 nm to form the seed layer 50 thereon. The surface of the seed layer 50 on each substrate 30 was cleaned and activated using sulfuric acid.

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Following the cleaning and activation of the seed layer 50, alternate layers of Co-Ni-Re-W-P 60 and of Cu 70 were formed, one after the other, on top of the seed layer 50 by electrochemical deposition methods. The methods used were electrolytic and electroless plating. In this way, the multi-layered material 20 was formed.

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The layers of Co-Ni-Re-W-P 60 were each deposited by electrolytic plating using a rotating disk electrode (RDE) system at a direct current density of 25 mA/cm^2 at room temperature. Platinum wire was used as the anode for plating each layer. An Ag/AgCl reference electrode was used as the reference electrode and was connected to the plating solution via a salt bridge. Electroplating was carried out at a rotational speed of 500rpm of the substrates 30 in order to achieve good uniformity of the layers deposited thereon.

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It is envisaged that the Cu layers 70 may be deposited on the magnetisable Co-Ni-Re-W-P layers 60 by either electrolytic or electroless plating from Cu electrolyte solution. When electrolytically plated, a direct current density of 25 mA/cm^2 and a rotational speed of 500 rpm were used in order to be consistent with the conditions for electroplating the Co-Ni-Re-W-P as described above. Thus, this electrolytic plating was carried out using a RDE under room temperature and using platinum as the anode. The Ag/AgCl reference electrode was again used as the reference electrode and was connected to the Cu plating solution via a salt bridge.

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To investigate a simplification of the present multi-layer plating procedure, electroless plating of Cu on Co-Ni-Re-W-P was carried out for comparison study. The process procedure for electroless plating was much simpler in comparison to the electrolytic plating of Cu since no current source was required. After electroplating of each Co-Ni-Re-W-P layer 60, the relevant substrate 30 was simply immersed in the Cu electrolyte solution for a controlled duration to have Cu electrolessly plated on the Co-Ni-Re-W-P.

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The multi-layered material resulting from the electrolytic plating of the Cu layers 70 will hereinafter be referred to as “multi-layer 1” or “ML1”; and the multi-layered material

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resulting from the electroless plating of the Cu layers 70 will be referred to as “multi-layer 2” or “ML2”.

The thickness of each magnetiseable Co-Ni-Re-W-P layer 60 was adjusted by controlling the electroplating time. Figure 2 is a graph of the relationship between the thickness of a deposited Co-Ni-Re-W-P layer as a result of the electrolytic plating method described above, against the duration of electrolytic plating bringing about that layer. As can be seen from Figure 2, the thickness of the Co-Ni-Re-W-P varies almost linearly with electroplating time, for the same electroplating conditions. It was observed that at a current density of 25 mA/cm² and agitation speed of 500 rpm, Co-Ni-Re-W-P was deposited at a rate of approximately 0.45 µm/min. Hence, by controlling the duration of the electroplating operation, layer thickness could be easily controlled. As is shown in Table 1, the Co-Ni-Re-W-P layers 60 were electroplated for the same duration of 120 seconds, regardless of whether or not these were layers in the ML1 or ML2 material; in other words, regardless of whether or not the associated Cu layers 70 were electrolytically plated or electrolessly plated. As a result, the film thickness of each magnetiseable layer 60 of Co-Ni-Re-W-P was substantially the same. Each Cu interlayer 70 was plated for 60 seconds, again, regardless of whether or not these were electrolytically plated layers 70 of ML1 or electrolessly plated layers of ML2. For comparison, a thin single layer of Co-Ni-Re-W-P and a separate thick single layer of Co-Ni-Re-W-P were electroplated from bath solution at 25mA/cm² and 500rpm for 120 and 720 (i.e. 120 x 6) seconds respectively. These single layer comparison materials are not referred to in Table 1.

Layers	Electro/Electroless Plating Time (s)	
	Multilayer 1 (ML1)	Multilayer 2 (ML2)
CoNiReWP-1	120 (E)	120 (E)
Cu-1	60 (E)	60 (EL)
CoNiReWP-2	120 (E)	120 (E)
Cu-2	60 (E)	60 (EL)
CoNiReWP-3	120 (E)	120 (E)
Cu-3	60 (E)	60 (EL)
CoNiReWP-4	120 (E)	120 (E)
Cu-4	60 (E)	60 (EL)
CoNiReWP-5	120 (E)	120 (E)
Cu-5	60 (E)	60 (EL)
CoNiReWP-6	120 (E)	120 (E)

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Table 1: Plating time for Co-Ni-Re-W-P/Cu multi-layers.

(Electroplating at 25mA/cm² and 500rpm is denoted as E, Electroless plating is denoted as EL).

Magnetic properties of samples were measured by using a vibrating sample magnetometer (VSM). Table 2 summarizes the absolute saturation magnetization M_s , absolute remanent magnetization M_r , coercivity H_c , and squareness S (M_s/M_r) in the out-of-plane (vertical) direction, both before and after annealing in ambient atmosphere at 200°C for 2 hours. It was observed that while M_s , M_r , H_c and S for the thin Co-Ni-Re-W-P single layer comparison material were slightly improved after annealing, the thick single layer comparison material exhibited a drastic drop in M_r , H_c and S after annealing at the same temperature. This was accompanied by a narrowing of the out-of-plane hysteresis curve as shown in the M-H plots of Figure 3, wherein M is the out-of-plane absolute magnetisation of the material and H is the strength of a magnetic field applied from an external source. In contrast, such drastic narrowing of hysteresis curve after annealing was not observed for the thin single layer comparison material. This is clear from the M-H curve shown in Figure 4. The same is true of the multi-layered materials 20, as is shown by the M-H curves in Figure

5. In other words, the multi-layered structures maintained a much higher M_r , H_c and S after annealing than did the thick single layer comparison material. It is believed that the different thermal behaviour is related to the thickness of the Co-Ni-Re-W-P films.

Magnetic properties deteriorated due to annealing when the film was thick at approximately

5 5.1 μm as shown in Figure 7. On the other hand, magnetic properties did not deteriorate but slightly improved when the film was thin at approximately 1.4 μm as shown in Figure 6.

Hence, by keeping each Co-Ni-Re-W-P layers in the multi-layered materials thin at approximately 1 μm as shown in Figures 8 and 9, thermal degradation of magnetic properties can be avoided.

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Samples		M_s (memu)	M_r (memu)	H_c (Oe)	S
Thin Single-Layer (~1.4 μm)	Un-annealed	60.7	14.3	2066.77	0.24
	Annealed	62.4	15.9	2210.08	0.26
Thick Single-Layer (~5.1 μm)	Un-annealed	376.5	88.0	2191.82	0.23
	Annealed	363.8	22.2	538.31	0.06
Multi-Layers (ML1) (Electroplated Cu)	Un-annealed	280.4	72.5	1999.80	0.26
	Annealed	273.8	65.4	1797.01	0.24
Multi-Layers (ML2) (Electroless plated Cu)	Un-annealed	270.0	68.4	1957.57	0.25
	Annealed	263.0	68.7	1980.75	0.26

Table 2: Out-of-plane Magnetic Properties of Co-Ni-Re-W-P single and multi-layers.

15 A comparison between magnetic properties after annealing of, on the one hand, the ML1 material containing the electrolytically plated Cu layers and, on the other hand, the ML2 material containing the electrolessly plated Cu layers shows that the ML2 material exhibited better thermal stability. There was a slight drop in M_r and H_c of the ML1 material with Cu layers that were electrolytically plated, whilst there was a slight

20 improvement in the same properties of the ML2 material in which the Cu layers were electrolessly plated. These differences could be due to the differences in the thickness of the Cu layers in the ML1 material formed as a result of electrolytic plating and the of the Cu layers in the ML2 material formed as a result of the electroless plating. This difference of thickness is apparent from the SEM images shown in Figures 8 and 9. Even though the

duration of the electrolytic plating used to form each of the Cu layers in the ML1 material was the same as the duration of the electroless plating used in the ML2 material (60 seconds), the electroless deposition of Cu was much slower and resulted in much thinner Cu layers and hence better thermal stability than did the electrolytic deposition.

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It is envisaged that in another embodiment of this invention, non-magnetiseable, electrically-conductive layers of Au may be substituted for those of Cu in the first embodiment described hereinabove.

10 In a further embodiment of this invention, an alternative multi-layered material (not shown) is provided. The alternative multi-layered material is substantially the same as that described above with reference to Figure 1, but differs in substituting magnetiseable layers of Co-Pt-P for the magnetiseable layers of Co-Ni-Re-W-P, and in substituting non-magnetiseable layers of Au for the non-magnetiseable layers of Cu. Although Au is used in
15 this alternative material as a non-magnetiseable layer between magnetiseable layers of Co-Pt-P, the observations made hereinabove in relation to electrolytic and electroless plating of non-magnetiseable layers apply equally in relation to the alternative material of this other embodiment. It is envisaged that the Co-Pt-P material may be the material whose composition and manufacture is described in Singapore Patent Application No. 200500445-

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CLAIMS

1. A multi-layered material for use in a microelectromechanical system (MEMS) device,
the material including a plurality of layers of a magnetiseable material comprising cobalt,
5 nickel, rhenium, tungsten and phosphorous (Co-Ni-Re-W-P), the or each adjacent pair of
layers of Co-Ni-Re-W-P having a respective layer of a non-magnetiseable, electrically-
conductive material therebetween.
2. A multi-layered material for use in a microelectromechanical system (MEMS) device,
10 the material including a plurality of layers of a magnetiseable material comprising cobalt,
platinum and phosphorous (Co-Pt-P), the or each adjacent pair of layers of Co-Pt-P having
a respective layer of a non-magnetiseable, electrically-conductive material therebetween.
3. A material according to claim 1 or claim 2, wherein the multi-layered material includes
15 at least five layers of the magnetiseable material, each such layer being spaced from the or
each adjacent layer of the magnetiseable material by a respective layer of the non-
magnetiseable, electrically-conductive material therebetween.
4. A material according to claim 3, wherein there are between five and ten of the layers of
20 magnetiseable material.
5. A material according to any preceding claim, wherein the material includes a base layer
of the, or of another, non-magnetiseable, electrically-conductive material, the base layer
acting as a seed layer for binding the remainder of the multi-layered material to a substrate
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6. A material according to claim 5, wherein a layer of Cr is be provided between the base
layer and the substrate.
7. A material according to claim 6, wherein the Cr layer has a thickness of approximately
30 20 nm.

8. A material according to any one of claims 4 to 7, wherein the base layer is approximately 200 nm thick.
9. A material according to any preceding claim, wherein each of the layers of magnetiseable material has a thickness in the range of 0.1 μm to 2 μm .
10. A material according to claim 9, wherein each of the layers of magnetiseable material has a thickness in the range of 0.5 μm to 1.5 μm .
11. A material according to any preceding claim, wherein each layer of the non-magnetiseable, electrically-conductive material that is disposed between a respective adjacent pair of the layers of magnetiseable material has a thickness in the range of 0.1 μm to 0.5 μm .
12. A material according to any preceding claim, wherein the non-magnetiseable, electrically-conductive material is Au or Cu.
13. A material according to claim 1 of any preceding claim when dependent on claim 1, wherein the non-magnetiseable, electrically-conductive material that is between adjacent pairs of layers of Co-Ni-Re-W-P is Cu.
14. A material according to claim 2 or any one of claims 3 to 11 when dependent on claim 2 wherein, the non-magnetiseable, electrically-conductive material that is between adjacent pairs of layers of Co-Pt-P is Au.
15. A microelectromechanical system (MEMS) device including a multi-layer material according to any preceding claim.
16. A multi-layered material for use in a microelectromechanical system (MEMS) device, the material including a plurality of layers of magnetiseable material, the or each adjacent pair of layers of magnetiseable material having a respective layer of a non-magnetiseable,

electrically-conductive material therebetween, wherein at least the layers of magnetiseable material are of a thickness of 0.1 and 2 μm .

17. A material according to claim 16, wherein the magnetiseable material comprises cobalt,
5 nickel, rhenium, tungsten and phosphorous (Co-Ni-Re-W-P).

18. A material according to claim 16, wherein the magnetiseable material comprises cobalt,
platinum and phosphorous (Co-Pt-P).

19. A material according to any one of claims 16 to 18, wherein the layers of magnetiseable
10 material are of a thickness in the range of 0.5 to 1.5 μm .

20. A method of manufacturing a multi-layered material for use in a
microelectromechanical system (MEMS) device, the method including the steps of forming
15 a plurality of layers of magnetiseable material, and a plurality of layers of non-
magnetiseable, electrically-conductive material, the various layers formed one on top of
another and alternately, with the or each adjacent pair of layers of magnetiseable material
having a respective layer of non-magnetiseable, electrically-conductive material formed
therebetween.

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21. A method according to claim 20, wherein the layers of magnetiseable material are of
cobalt, nickel, rhenium, tungsten and phosphorous (Co-Ni-Re-W-P).

22. A method according to claim 20, wherein the layers of magnetiseable material are of
25 cobalt, platinum and phosphorous (Co-Pt-P).

23. A method according to any one of claims 20 to 22, wherein the method includes the
step of forming the layers of magnetiseable material by electrolytic plating.

24. A method according to any one of claims 20 to 23, wherein the method includes the step of forming the layers of non-magnetisable, electrically-conductive material by electroless plating.

5 25. A method according to any one of claims 20 to 24, wherein the method includes the step of placing a substrate on which the layers are to be formed into an electrochemical bath, whereby layers are formed on the substrate.

26. A method according to claim 25, wherein the bath is at a pH of or below 5.0.

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27. A method according to any one of claims 20 to 26, wherein the method includes forming each layer of magnetisable material to a thickness in the range of 0.1 to 2 μm .