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(54) **GMR NANOWIRE SENSORS**

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(51) **Int. Cl.**
G01B 7/14 (2006.01)
G01D 5/14 (2006.01)
G01R 33/09 (2006.01)

(52) **U.S. Cl.**
CPC ***G01B 7/14*** (2013.01); ***G01D 5/145*** (2013.01); *G01R 33/09* (2013.01)

(58) **Field of Classification Search**
CPC G01D 5/145; G01D 5/147; G01D 5/247; G01D 5/00; G01R 33/09; G01R 33/093; G01B 7/003; G01P 3/487; G01P 3/443; B60L 13/06; B60L 2200/26; H04L 12/2697; H04L 43/50
USPC 324/207.21, 207.22, 207.11, 219, 220; 977/742, 953
See application file for complete search history.

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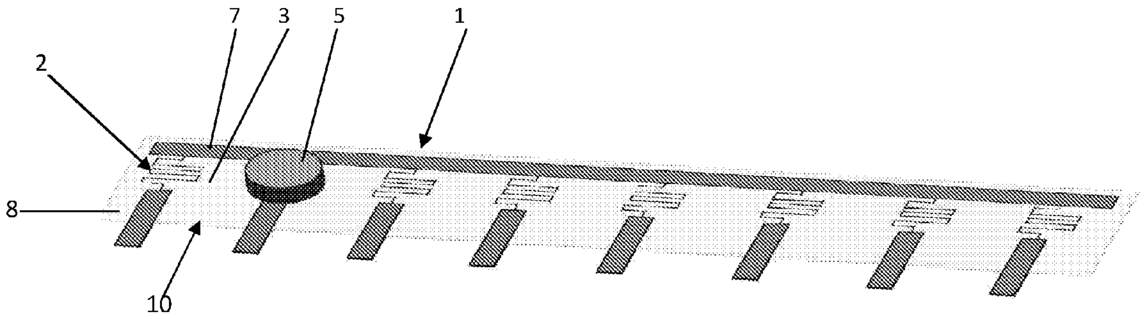
(57) **ABSTRACT**

A magnetic position sensor having at least one magnetic field sensor including a solidified layer of GMR nanowire carrier fluid formed on a substrate material. The solidified layer of carrier fluid has (i) discrete GMR nanowires each having a diameter of less than about 0.5 um and a length less than about 250 um; and (ii) a concentration of GMR nanowires in the dried layer between about 0.001 and about 10 percent by weight of the solution. The position sensor further includes a detection circuit capable of detecting a change in resistance of the magnetic field sensor.

23 Claims, 10 Drawing Sheets



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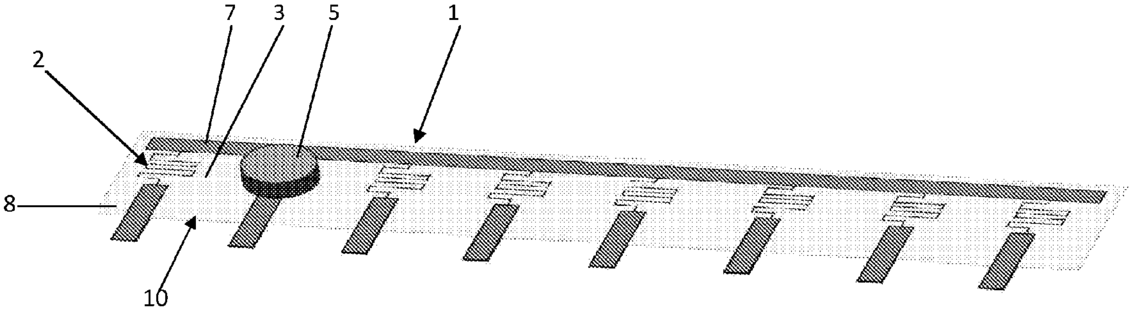
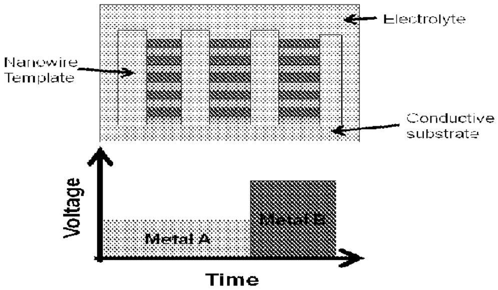


Figure 1



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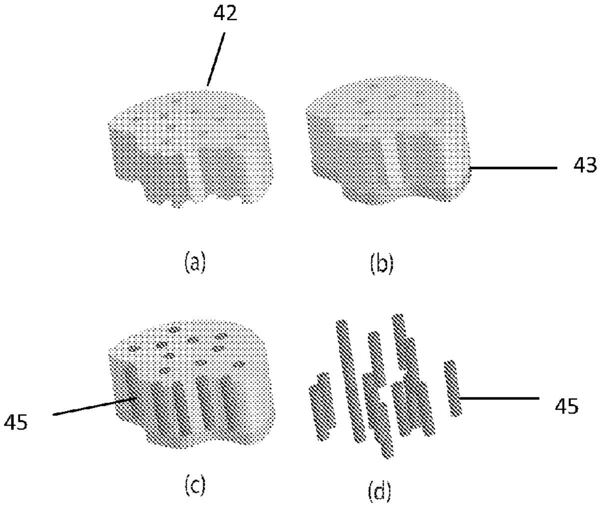

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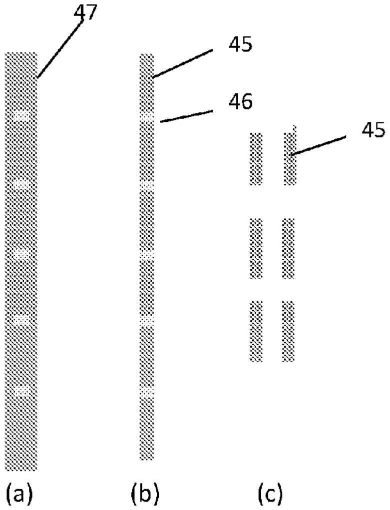

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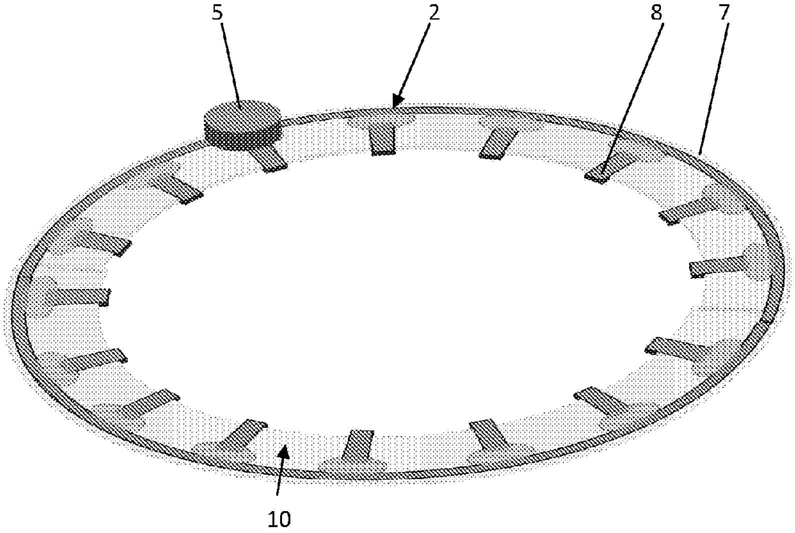

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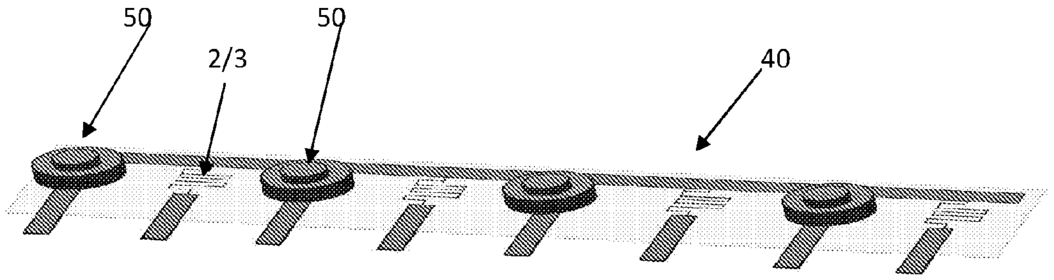

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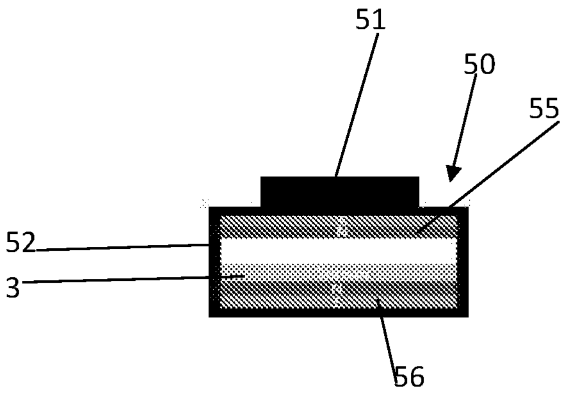

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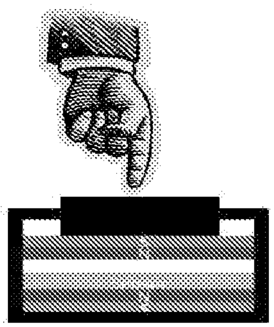

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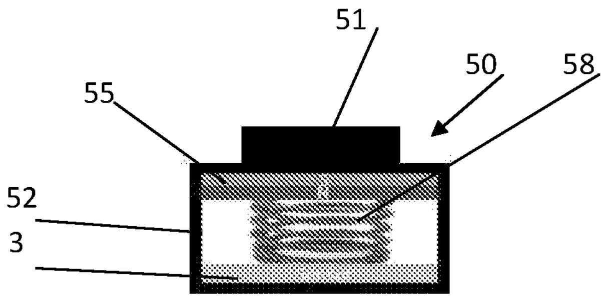

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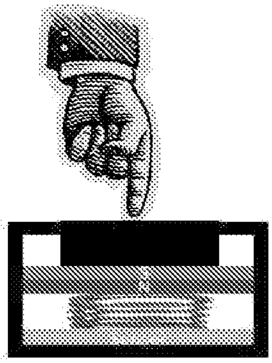

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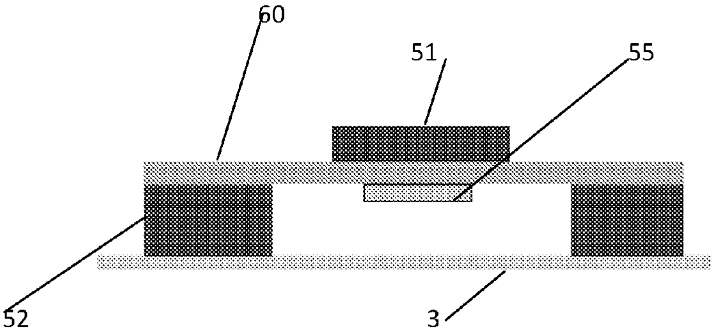

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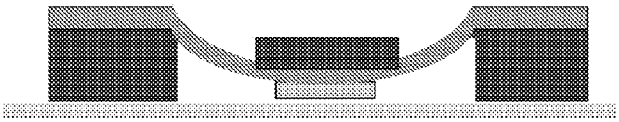

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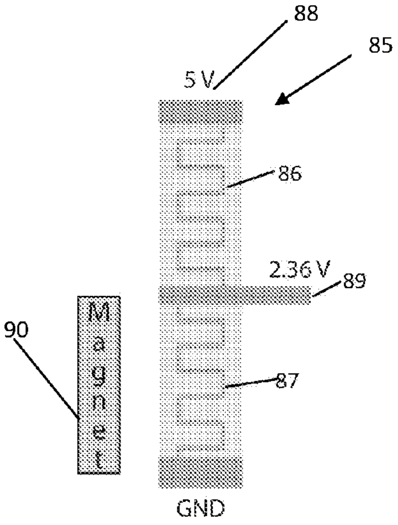

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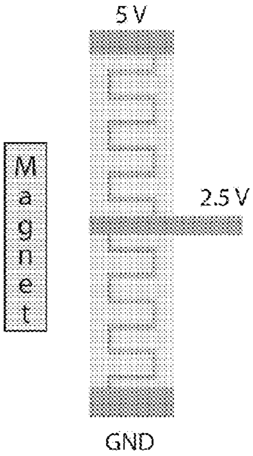

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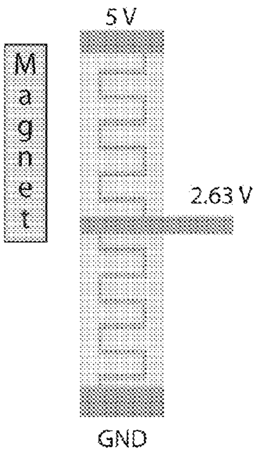

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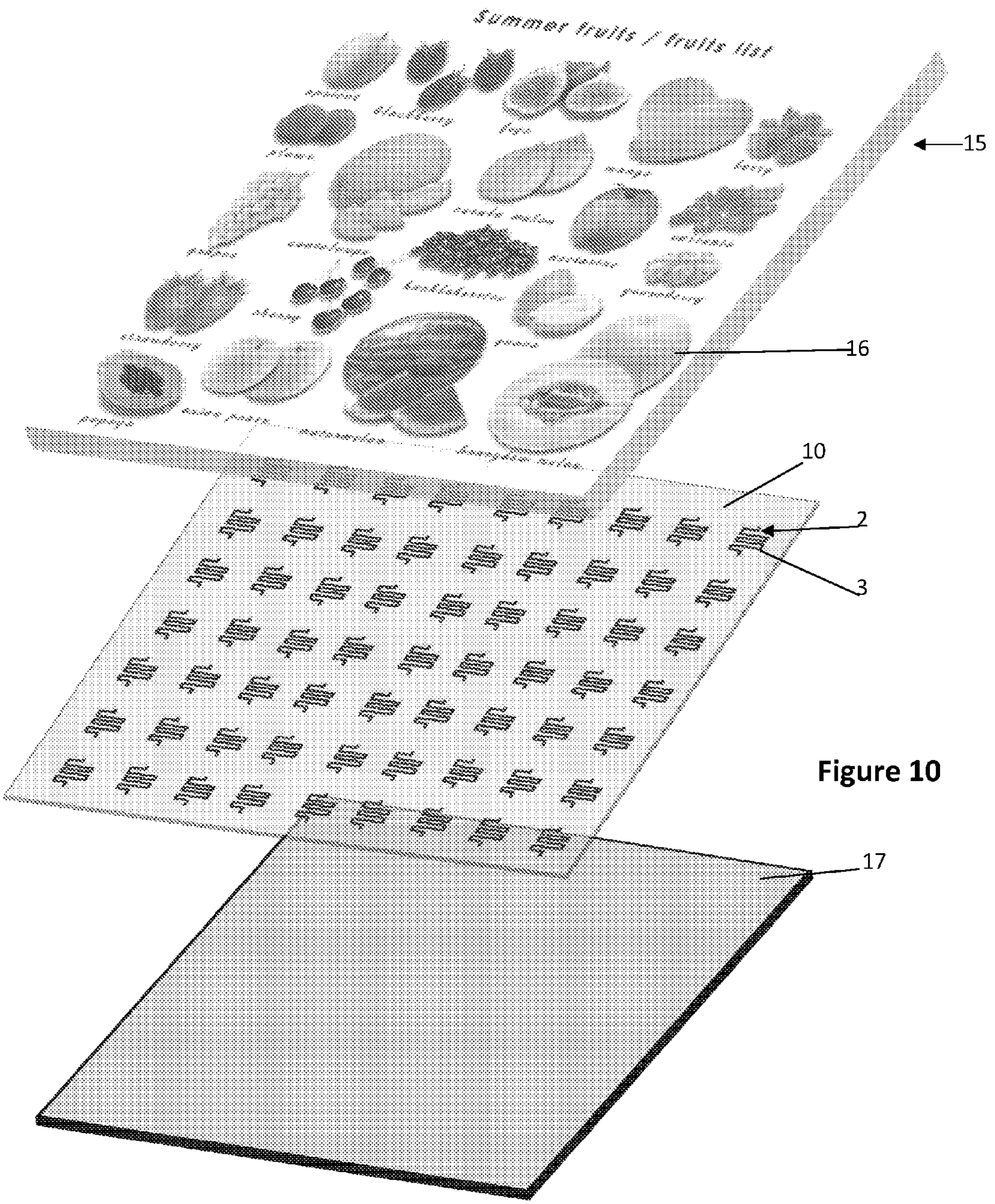
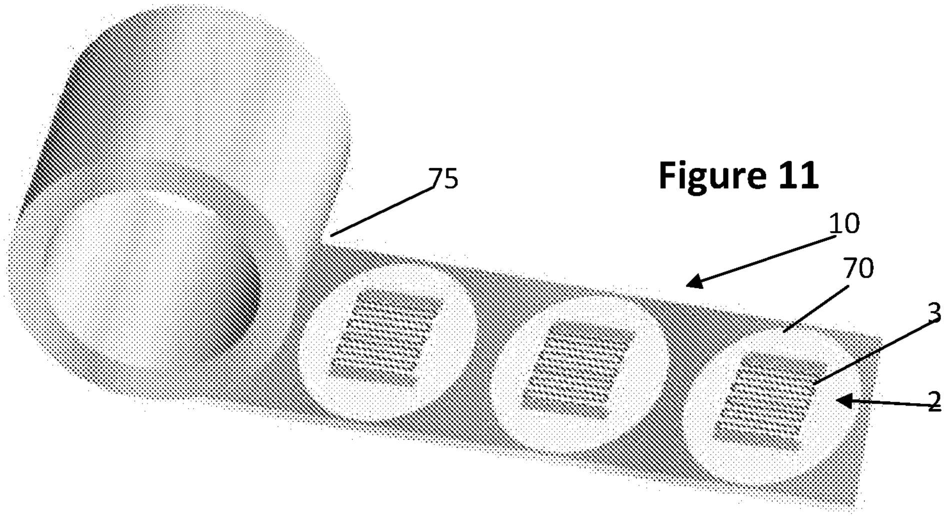
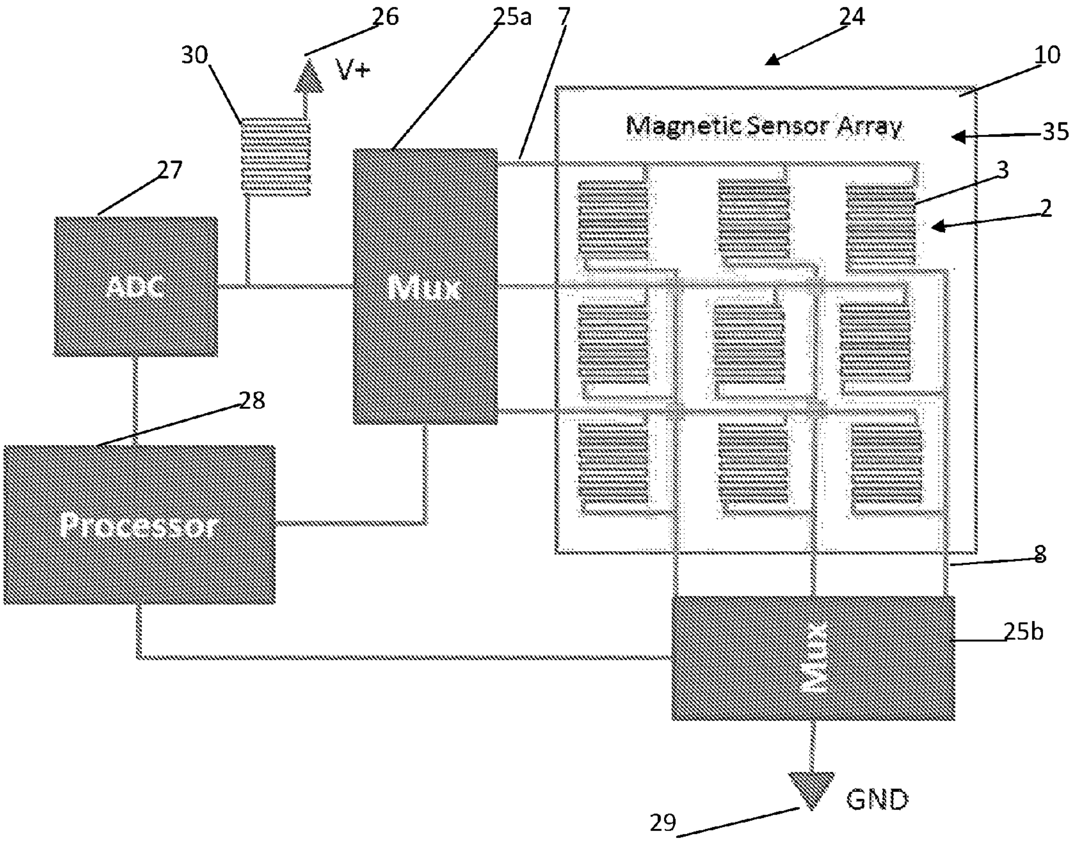


Figure 10

Figure 11




26
25a
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V+
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Magnetic Sensor Array
35
27
3
2
ADC
Mux
28
Processor
8
25b
Mux
GND
29

Figure 12

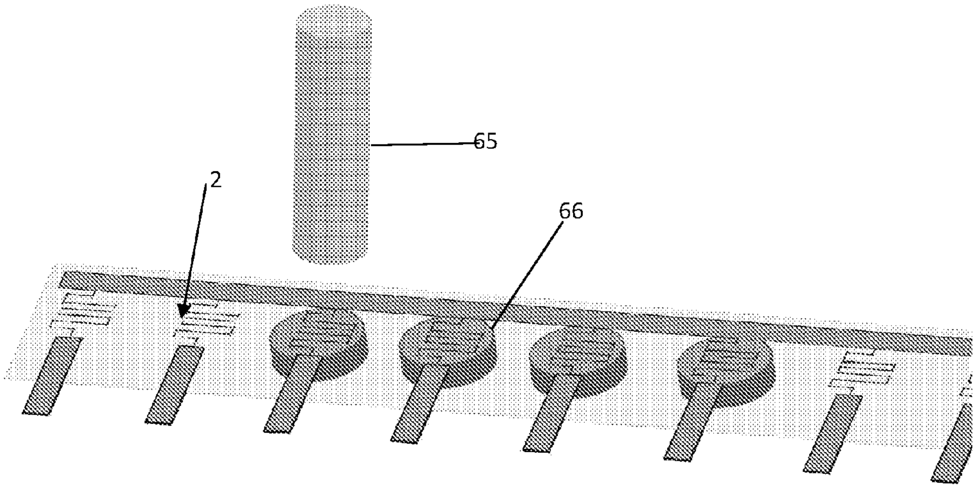

Figure 13

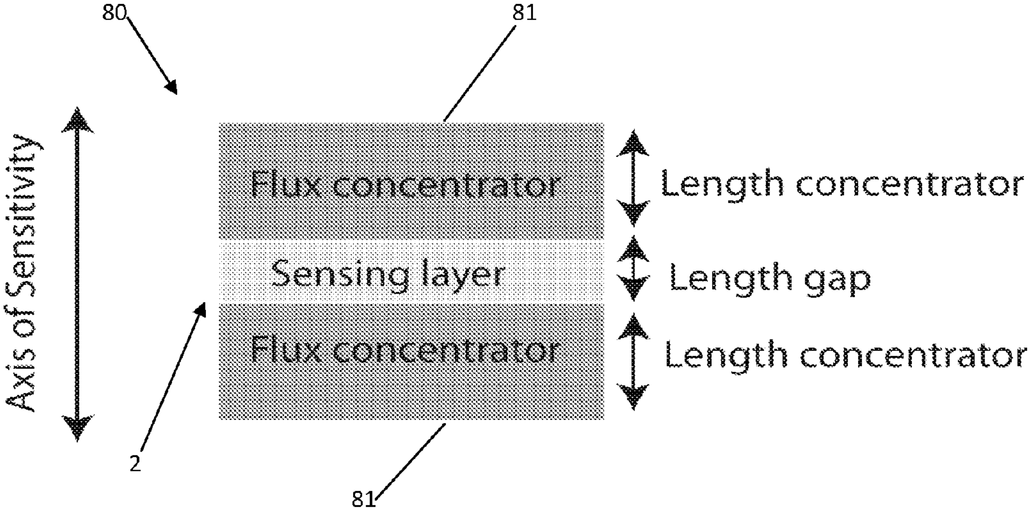

Figure 14

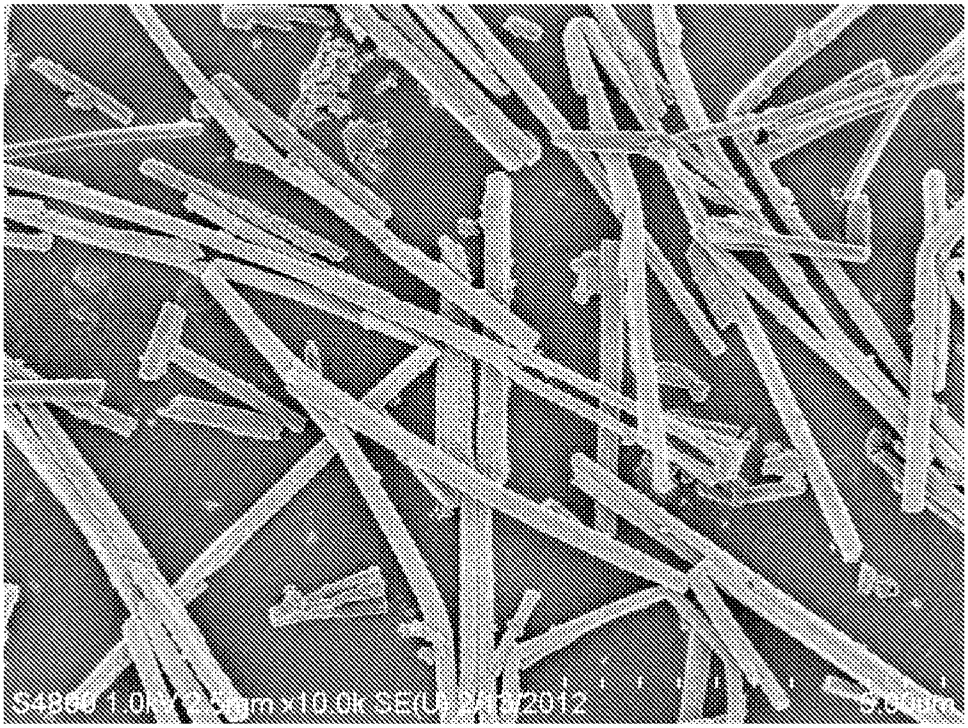

Figure 15

GMR NANOWIRE SENSORS

This application claims the benefit under 35 USC 119(e) of U.S. Provisional Application Ser. No. 61/622,605 filed Apr. 11, 2012, which is incorporated by reference herein in its entirety.

This invention was made with government support under grant number NNX10AI40H awarded by the National Aeronautics & Space Administration. The government has certain rights in the invention.

BACKGROUND OF INVENTION

Magnetoresistance (MR) is the property of a material to change its electrical resistance in the presence of a magnetic field. Magnetic sensors based on the MR effect can measure the strengths of magnetic fields or the relative direction of the fields. One of the most significant applications of MR sensors is their incorporation into read heads for magnetic recording devices. Five distinct types of MR are ordinary magnetoresistance (OMR), anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR), tunneling magnetoresistance (TMR) and colossal magnetoresistance (CMR).

There are two types of GMR geometries, which are named current in plane (CIP) and current perpendicular to the plane (CPP). Each geometry has a different quantum mechanical effect that changes the probability of conduction electrons scattering throughout their layers and consequently changing the electrical resistance of the GMR material. CIP GMR describes a geometry whereby the magnetic field must be applied in the same direction as the current flow for a change in resistance to be observed in the material and the change in the mean free path of conduction electrons determines the amount of resistance change. Alternatively, CPP GMR refers to a geometry typically having multilayers in high aspect ratio configurations. With CPP GMR, a magnetic field must be applied perpendicular to the current flow for resistance changes to be observed. The magnetic field alters the magnitude of the spin-flip diffusion length of conduction electrons, influencing the resistance change of the GMR material. CPP GMR performance is partially a function of the number of alternating material layers with a higher number of layers giving higher changes in resistances in magnetic fields.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** illustrates one embodiment of a one dimensional position sensor.

FIG. **2** illustrates one method of forming nanowires for use in the position sensors.

FIGS. **3**A and **3**B further illustrate methods of forming nanowires.

FIG. **4** illustrates a second embodiment of a one dimensional position sensor.

FIG. **5** illustrates a third embodiment of a one dimensional position sensor.

FIGS. **6**A and **6**B illustrate one embodiment of a push-button sensor.

FIGS. **7**A and **7**B illustrate a second embodiment of a push-button sensor.

FIGS. **8**A and **8**B illustrate a third embodiment of a push-button sensor.

FIGS. **9**A to **9**C illustrate a potentiometer type device.

FIG. **10** illustrates a two dimensional position sensor.

FIG. **11** illustrates sensor elements formed on a removable adhesive substrate.

FIG. **12** illustrates one embodiment of a sensor detection circuit.

FIG. **13** illustrates one embodiment of a ferromagnetic object sensor.

FIG. **14** illustrates one embodiment of a flux concentrator structure.

FIG. **15** is an SEM image of a solidified layer of GMR nanowires.

DETAILED DESCRIPTION OF SELECTED EMBODIMENTS

One embodiment of the present invention is a magnetic position sensor **1** such as illustrated in FIG. **1**. The position sensor **1** includes at least one, and more typically a series of, magnetic field sensors **2** formed on a substrate **10**. In this embodiment, the magnetic field sensors **2** are shaped as a serpentine line **3** of GMR nanowires formed upon substrate **10**. The ends of serpentine line **3** are connected to conductors **7** and **8** which ultimately will connect the magnetic field sensor **2** to a detection circuit. Although more detailed examples of detection circuits are provided below, the detection circuit will generally measure the resistance of the sensors. Two common resistance measurements include: first, by changing a resistance into a corresponding voltage for measurement purposes; and secondly, by placing the sensor in a RC circuit and measuring the charging and discharge rate of the capacitor.

In this embodiment, the serpentine lines **3** are approximately 0.5 mm to 1 mm wide, but may be narrower or wider, e.g., about 0.01 to 10 mm. The lines **3** are formed by adhering (e.g., drying or curing) a GMR nanowire carrier solution onto the substrate **10** in the pattern of the serpentine lines. The GMR nanowire carrier liquid adhered to or dried upon a substrate may be referred to as a solidified layer of GMR nanowires. As used herein, “nanowire” or “nanostructure” generally refers to small structures, at least one dimension of which (i.e., width or diameter) is less than 1000 nm, more typically, less than 500 nm or 100 nm or 50 nm. In various embodiments, the width or diameter of the nano structures are in the range of 10 to 40 nm, 20 to 40 nm, 5 to 20 nm, 10 to 30 nm, 40 to 60 nm, or 50 to 70 nm. The length of a nanowire may vary in different embodiments from less than 1 micron to several hundred microns. In many embodiments, the GMR nanowires in the carrier solution may have a diameter of less than about 0.5 um and a length less than about 200 um. More preferably, the GMR nanowires will have a diameter between about 10 nm and about 200 nm and a length between about 1 um and about 100 um. Of course, other specialized embodiments may have nanowire diameters greater than 0.5 um and lengths greater than 200 um. In many embodiments, the GMR nanowires will have an aspect ratio (i.e., length over diameter) of at least three and more preferably at least about 10, and still more preferably at least about 50. The term “nanowire” includes any elongated structure such as nanorods (solid nano structures) and nanotubes (hollow nanostructures), whether the cross-section is generally round or some other shape.

In many embodiments, the concentration of GMR nanowires within the carrier solution may be between about 0.005 and about 10 percent by weight of the solution, or any sub-range there between. In certain embodiments, the concentration of GMR nanowires within the carrier solution is between about 0.01 and about 1.5 percent. Naturally, other embodiments could be less than 0.01 or greater than 10 percent. When the dried GMR nanowire layer is formed on the substrate, the nanowires will generally be present in a quantity ranging from about 1,000 nanowires per mm^2 to about 50,000 nanowires per mm^2 or any subrange there between. As a general principle, the longer the nanowires, the fewer needed to form a connective nanowire network for magnetoresistance measurement. Again, particular embodiments could employ fewer than 100 nanowires per mm^2 or more than 5,000,000 mm^2 (or any subrange between these values).

The GMR nanowires are often suspended or dispersed in a carrier liquid to facilitate their deposition on the substrate. Typically, the GMR nanowires are at least temporarily suspended in the carrier fluid. However, the nanowires only need remain suspended long enough to be applied to the substrate material. Preferably, the carrier fluid should be homogeneous, i.e., the GMR nanowires should be suspended uniformly in the carrier solution. It is understood that, as used herein, "deposition" and "coating" are considered interchangeable. Any number of fluids may be used as the nanowire carrier fluid. For example, any non-corrosive liquid in which the GMR nanowires can form a stable dispersion may be used. Preferably, the GMR nanowires are dispersed in water, an alcohol, a ketone, ethers, hydrocarbons or an aromatic solvent (benzene, toluene, xylene, etc.). More preferably, the liquid is volatile, having a boiling point of no more than 200° C., no more than 150° C., or no more than 100° C.

In addition, the GMR nanowire carrier fluid (or "dispersion") may contain binders and other additives to control viscosity, corrosion, adhesion, and nanowire dispersion.

A binder may be any material or substance that holds or draws other materials together to form a cohesive whole. Binders may include gelling or thickening agents along with viscosity modifiers. Examples of suitable binders include, but are not limited to, carboxy methyl cellulose (CMC), 2-hydroxy ethyl cellulose (HEC), hydroxy propyl methyl cellulose (HPMC), methyl cellulose (MC), poly vinyl alcohol (PVA), tripropylene gylcol (TPG), and xanthan gum (XG).

Examples of suitable viscosity modifiers include biopolymers, such as hydroxypropyl methyl cellulose (HPMC), methyl cellulose, xanthan gum, tragacanth gum, carboxy methyl cellulose, and hydroxy ethyl cellulose; acrylic polymers, such as, sodium polyacrylate; and water-soluble synthetic polymers, such as, polyvinyl alcohol.

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. Examples of surfactants may include ethoxylates, alkoxylates, ethylene oxide and propylene oxide and their copolymers, sulfonates, sulfates, disulfonate salts, sulfosuccinates, phosphate esters, and fluorosurfactants (e.g., Zonyl® by DuPont). More particular examples of suitable surfactants include Zonyl® FSN, Zonyl® FSO, Zonyl® FSH, Triton (x100, x114, x45), Dynol (604, 607), n-Dodecyl b-D-maltoside and Novek.

In one example, the nanowire dispersion may include, by weight, from 0.0025% to 0.1% surfactant (e.g., a preferred range is from 0.0025% to 0.05% for Zonyl® FSO-100), from 0.02% to 4% viscosity modifier (e.g., a preferred range is 0.02% to 0.5% for HPMC), from 94.5% to 99.0% solvent and from 0.01% to 1.4% GMR nanowires.

Solvents help adjust the curing rate and viscosity of the solution in its liquid state. The solvents evaporate off as the solution dries. There are two types of carrier solutions: solvent-based and water-based. Examples of suitable solvents include alcohols, ketones, ethers, hydrocarbons or aromatic solvents (benzene, toluene, xylene, etc.) as mentioned above. The ratios of components of the dispersion may be modified depending on the substrate and the method of application used. The viscosity range of the GMR nanowire carrier liquid may vary greatly depending on the method of application, For inkjet printing applications, the viscosity can range from about 1 to about 40 cP; for gravure printing about 40 to about 200 cP; and for screen printing, over 1000 cP. Thus the viscosity may generally range from about 0.3 to about 2000 cP (or any subrange in between). One preferred viscosity range for the nanowire dispersion is between about 1 and 40 cP (or any subrange there between). Certain embodiments of the carrier fluid may include flux concentrator agents such as nanoparticles from an alloy consisting of cobalt, magnetite, or iron. Additional information on carrier fluids may be found in U.S. Pat. No. 8,174,667 which is incorporated by reference herein in its entirety

The GMR nanowires themselves are typically constructed by alternating ferromagnetic and non-magnetic conductive layers. Typically, these will be CPP GMR nanostructures In certain embodiments, the ferromagnetic conductive layers are less than 100 nm (in one example 15 nm) in thickness and non-magnetic conductive layers are less than 50 nm (in one example 5 nm) in thickness. The GMR nanowires comprise at least 2 alternating ferromagnetic and non-magnetic conductive layers, and more typically, will comprise tens, hundreds, or even thousands of alternating layers. While many embodiments of the GMR nanowires will have at least 5, 10, 25, or 50 alternating layers, certain embodiments could have fewer alternating layers. Example compounds forming the ferromagnetic layer may include Co, CoFe, CoNiFe, CoNi, CoNiFeCr, CoCr, CoNiCr, NiFe, NiCo, or NiCoCr. Example materials forming the non-magnetic conductive layer include Cu, Ag, Au or alloys of these metals. One particular example of a GMR structure is disclosed in U.S. Pat. No. 7,016,168 which is incorporated by reference herein in its entirety. In this example, the GMR structure includes a seed layer; a pinning layer formed of an antiferromagnetic material formed on the seed layer; and a synthetic antiferromagnetic pinned layer formed on the pinning layer. The pinned layer further comprises: a first ferromagnetic layer; an antiferromagnetically coupling layer formed on the first ferromagnetic layer; a second ferromagnetic layer formed on the coupling layer; and wherein the magnetizations of the first and second ferromagnetic layers are antiparallel. In this embodiment, the first ferromagnetic layer is a layer of CoFe formed to a thickness between approximately 20 and 60 angstroms; the second ferromagnetic layer is a layer of CoFe formed to a thickness between approximately 20 and 60 angstroms; and the coupling layer is a layer of Ru formed to a thickness between approximately 6 and 9 angstroms. Naturally, the above is merely one example of an acceptable GMR structure and many conventional or future developed GMR structures may be employed in the present invention. Likewise, the GMR nanowires could be formed by any number of conventional or future developed fabrication techniques. One illustrative example suggested in FIG. **3**A is a method including the steps of (a) providing a substrate such as a anodized aluminum oxide (AAO) membrane **42** with nano size pores, i.e., pores less than about 0.5 um in diameter and at least 1 μm in depth; (b) making one side of the AAO membrane conductive by applying a conductive material **43**, (c) forming alternating ferromagnetic and non-magnetic conductive layers within the pores; and (d) dissolving the AAO membrane in order to release the GMR nanowires **45**.

This method is a template assisted nanowire fabrication technique. The template (i.e., the AAO membrane) has many nano size pores that serve as a mold for the formation of a single nanowire. AAO membranes are used as templates in many nanotechnology applications to eliminate the need for expensive lithographical techniques. The formation of the nanoporous AAO membranes is done by an electro-chemical process that changes the surface chemistry of the metal, by oxidation, resulting in an anodic oxide layer. By tightly controlling the pH of the electrolyte and voltage used during the AAO fabrication, highly ordered arrays of cylindrical shaped nanopores can be formed with well-regulated pore diameters, periodicities and density distributions.

Usually the bottom of the template is made conductive by sputtering on a metal, such as gold, in order to form a base substrate for the formation of nanowires. Although many different materials may be used for the template, e.g. polycarbonate membranes, preferred embodiments include anodized aluminum oxide membrane templates because they possessed a higher uniformity of pores at a higher density. For example, the aluminum oxide pore sizes may range from 10 nm-200 nm, with a pore density of 9×10^8 to 2×10^{11} pores/cm^2, and an aluminum oxide film thickness of about 15 μm to 150 μm.

As referenced above, the substrate was made conductive by sputtering a gold layer and this allows the deposition of nanowires into the template through an electrodeposition or electroplating process. FIG. **2** suggests the pores of a membrane template with the conductive substrate serving as a cathode. The membrane is connected as a cathode in a standard electrochemical setup with the template, anode, cathode, and reference electrode positioned in an electrolyte solution containing ions of the metals to be deposited. When a constant DC voltage is applied in the electroplating process, metal ions from the electrolyte solution will travel inside the nanopores and bond with the substrate and as the deposition continues to take place, metal nanowires are formed inside the pores.

Formation of GMR nanowires typically requires the electroplating multilayers of two or more separate metals or alloys within the template. Deposition of multilayers from one electrolyte solution may be accomplished by choosing metals with high differences in standard electrode potentials. To overcome the problem of depositing alloys instead of pure metals in electrodeposited multilayer materials, the electrolyte solution should contain only traces of metal A ions with a high concentration of metal B ions (assuming that metal A has a higher standard electrode potential than metal B). At an adequately low polarization potential the rate of deposition of metal B is high while the rate of deposition of metal A is slow because it is controlled by diffusion. When the potential is at a considerably less negative polarization potential, only metal A is deposited. As the potential is cycled between the two potentials, multilayers of substantially pure metal A and metal B with traces of metal A are formed, as suggested in FIG. **2**.

In this embodiment, a pulsing potential electrodeposition technique scheme was used to electrodeposit the multilayer GMR nanowires. In one example, in order to ensure that the layers that are deposited are flat, a copper base is formed at the bottom of the membrane by keeping the potential at −0.25 V for 2 hrs. However, in other examples, nanowires have been produced by keeping the potential at −0.25 V for a much shorter time, e.g., 15 minutes. After the Cu base is formed, the multilayers are deposited by first keeping the potential at −0.35 V until a total amount of 0.005 C of charge passed through the cathode for copper layers and then changing the potential to −2.2 V for 0.01 C of charge for the alloy (e.g., CoNiFeCu) layers. After deposition of the alloy layer, the potentiostat is transitioned into open circuit to prevent severe alloy dissolution during the copper deposition cycle that could damage the interfaces and leave the alloy layer thickness inexact. Following the open circuit interruption, the entire cycle is repeated over again starting with the copper layer. The length of the nanowires depended on the number of cycles performed during electrodeposition. On average, it took 30 s for a copper layer, less than is for an alloy layer, and 5 s for the open circuit stage for a total of 36 s for a complete cycle. Combing the 2 hrs for the copper base at the beginning of the fabrication process with the deposition of the multilayers, it took 17 hrs to form GMR nanowires having 1,500 layers.

After GMR nanowires of the selected metals are electrodeposited into the pores of the anodized aluminum oxide (AAO) membrane templates, the conductive bottom layer can be removed and the template can be dissolved with strong base freeing the nanowires. After the template is completely dissolved, the nanowires can then be rinsed and suspended in a carrier solution, such as DI water or isopropyl alcohol. When the nanowires are needed for further fabrication steps, ultrasonication may be used to better disperse the nanowires within the carrier solution.

Although electrodeposition within a template is described above, many different techniques could be used to create the nanowires. For example, chemical processes such as chemical vapor deposition (CVD) techniques. Alternatively, physical vapor deposition techniques could be employed, including evaporation (deposition) procedures such as (i) molecular beam epitaxy (MBE), (ii) electron beam epitaxy, or (iii) ion plating. Likewise, sputtering procedures could be used, such as (i) ion-beam sputtering, (ii) RF magnetron sputtering, or (iii) DC magnetron sputtering.

Using a template assisted fabrication method typically produces a single nanowire per pore of the template. The length of the formed nanowire is either the same as the thickness of the template or shorter. However, in certain embodiments, it may be disadvantageous to use long nanowires for magnetic sensors due to the method of applying the GMR nanowire carrier fluid. For instance, particle sizes over 2 μm may tend to clog an inkjet printer. If the length of the nanowires must be shorter, the density of nanowires must increase for conductivity and, the densities should increase exponentially when the length of the nanowires decreases linearly in order to achieve the same degree of connectivity of the nanowires.

As one solution to this difficulty, multiple smaller multilayer GMR nanowires may be created by stacking them inside a single pore as suggested in FIG. **3**B. Stacking of the multilayer GMR nanowires can be accomplished by electrodepositing a sacrificial etch layer **46** (e.g., gold) between multilayer GMR nanowires. Once the template **47** is removed, the etch layer **46** can be dissolved away leaving the multilayer GMR nanowires **45**. FIG. **3**B shows (a) a pore with multiple multilayer GMR nanowires separated by the sacrificial etch layer, (b) the template dissolved, and (c) the sacrificial etch layers removed, creating a series of smaller nanowires.

In other embodiments, the multilayer GMR nanowires can be fabricated from multiple electrolyte baths, including one electrolyte for the ferromagnetic layer and a separate electrolyte bath for the nonmagnetic conductive layer. The GMR template can be transferred between baths either manually or through a robotic process. Likewise, the GMR nanowires may be produced by other techniques which do not necessarily employ a template.

As used herein, “substrate” refers to a material onto which the GMR nanowire layer is positioned or formed onto, whether directly or indirectly. The substrate can be rigid or flexible, clear or opaque. Suitable rigid substrates include, for example, silicon, glass, polycarbonates, acrylics, and the like. Suitable flexible substrates include, but are not limited to: polyesters (e.g., polyethylene terephthalate (PET), polyester naphthalate, and polycarbonate), polyolefins (e.g., linear, branched, and cyclic polyolefins), polyvinyls (e.g., polyvinyl chloride, polyvinylidene chloride, polyvinyl acetals, polystyrene, polyacrylates, and the like), cellulose ester bases (e.g., cellulose triacetate, cellulose acetate), polysulphones such as polyethersulphone, polyimides, silicones and other conventional polymeric films. Additional examples of suitable substrates can be found in U.S. Pat. No. 6,975,067 which is incorporated by reference herein.

In certain embodiments, the substrate may be functionalized to better receive GMR nanowires. Examples of functionalizing compounds may include 3-aminopropyltriethoxysilane (APTES), carboxylic acids, or self-assembled monolayers (SAMs). Example SAM materials include oleic acid, tetramethylammonium hydroxide, citric acid, soy lecithin, sodium dodecyl sulfate, perfluorodecyltrichlorosilane (FDTS), octadecyltrichlorosilane (OTS), polyethylene oxide (PEO), and Triton X-100 (TX-100), and polyvinyl alcohol (PVA). Various conventional or future developed techniques may be used to prevent or reduce corrosion of the GMR nanowires which would otherwise reduce magneto-resistance properties. For example, a "barrier layer" could be formed on the layer of GMR nanowires adhered to the substrate. "Barrier layer" refers to a layer that reduces or prevents gas or fluid permeation into the GMR nanowire layer. Barrier layers are well known in the art, including without limitation: see, e.g. U.S. Patent Application No. 2004/0253463, U.S. Pat. Nos. 5,560,998 and 4,927,689, EP Patent No. 132,565, and JP Patent No. 57,061,025. Furthermore, a protective film above the GMR nanowires may act as a barrier layer. For example, the protective film could be flexible and made of the same material as a flexible substrate on which the GMR nanowires positioned. Examples of protective films include, but are not limited to: polyester, polyethylene terephthalate (PET), polybutylene terephthalate, polymethyl methacrylate (PMMA), acrylic resin, polycarbonate (PC), polystyrene, triacetate (TAO), polyvinyl alcohol, polyvinyl chloride, polyvinylidene chloride, polyethylene, ethylene-vinyl acetate copolymers, polyvinyl butyral, metal ion-crosslinked ethylene-methacrylic acid copolymers, polyurethane, cellophane, polyolefins or the like; particularly preferable are PET, PC, PMMA, or TAO because of their high strength.

In other embodiments, GMR sensor structure may include other types of corrosion inhibitors, in addition to, or in lieu of the barrier layer as described above. Different corrosion inhibitors may provide protection to the metal nanowires based on different mechanisms. According to one mechanism, the corrosion inhibitor binds readily to the GMR nanowires, forming a protective film on a metal surface. These are also referred to as barrier-forming corrosion inhibitors. In one embodiment, the barrier-forming corrosion inhibitor includes certain nitrogen-containing and sulfur-containing organic compounds, such as aromatic triazoles, imidazoles and thiazoles. These compounds have been demonstrated to form stable complexes on a metal surface to provide a barrier between the metal and its environment. For example, benzotriazole (BTA) is a common organic corrosion inhibitor for copper or copper alloys. Alkyl substituted benzotriazoles, such as tolytriazole and butyl benzyl triazole, can also be used. (See, e.g., U.S. Pat. No. 5,270,364.) Additional suitable examples of corrosion inhibitors include, but are not limited to: 2-aminopyrimidine, 5,6-dimethylbenzimidazole, 2-amino-5-mercapto-1,3,4-thiadiazole, 2-mercaptopyrimidine, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, and 2-mercaptobenzimidazole.

Another class of barrier-forming corrosion inhibitors includes biomolecules that show a particular affinity to the metal surface. These include small biomolecules, e.g. cysteine, and synthetic peptides and protein scaffolds with fused peptide sequences with affinity for metals; see, e.g. U.S. application Ser. Nos. 10/654,623, 10/665,721, 10/965,227, 10/976,179, and 11/280,986, U.S. Provisional Application Ser. Nos. 60/680,491, 60/707,675 and 60/680,491.

Other barrier-forming corrosion inhibitors include dithiothiadiazole, alkyl dithiothiadiazoles and alkylthiols, alkyl being a saturated C_6-C_{24} straight hydrocarbon chain. This type of corrosion inhibitor can self-assemble on a metal surface to form a monolayer, thereby protecting the metal surface from corroding.

According to another mechanism, a corrosion inhibitor binds more readily with a corrosive element (e.g., H_2S) than with the metal nanowires. These corrosion inhibitors are known as "scavengers" or "getters", which compete with the metal and sequester the corrosive elements. Examples of H_2S scavengers include, but are not limited to: acrolein, glyoxal, triazine, and n-chlorosuccinimide. (See, e.g., Published U.S. Application No. 2006/0006120.) In certain embodiments, the corrosion inhibitor (e.g., H_2S scavengers) can be dispersed in the matrix provided its presence does not adversely affect the optical or electrical properties of the GMR nanowire layer.

In other embodiments, the GMR nanowires can be pretreated with a corrosion inhibitor before or after being deposited on the substrate. For example, the metal nanowires can be pre-coated with a barrier-forming corrosion inhibitor, e.g., BTA and dithiothiadiazole. In addition, the metal nanowires can also be treated with an anti-tarnish solution. Metal anti-tarnish treatments are known in the art. Specific treatments targeting H_2S corrosion are described in, e.g., U.S. Pat. No. 4,083,945, and U.S. Published Application No. 2005/0148480.

In yet other embodiments, the metal nanowires can be alloyed or plated with another metal less susceptible to corrosive substances found in the nanowire's manufacturing or end-use environment. For example, adding chromium to the alloy layer should help prevent oxidation of nanowires. Likewise, using a copper gold alloy for the conductive layer should lessen the susceptibility to oxidation.

In still further embodiments, oxidation of the GMR nanowires introduced during fabrication may be reduced or removed once the carrier fluid is applied to and dried upon the substrate (depending on the nature of the matrix forming the GMR nanowire layer). Oxidation can be removed with most acids including, HCL, acetic acid, or nitric acid. Alternatively, oxidation may be removed by placing the nanowires in a reducing atmosphere, e.g., hydrogen or nitrogen.

In certain embodiments, it will be desirable for the GMR nanowire sensor layer to be substantially transparent. It will be understood that the transparency of the nanowire layer will be affected by, among other factors, the loading of nanowires therein. Likewise, higher aspect ratio nanowires allow for the formation of a sensor with a less dense network of nanowires leading to a lesser impact on optical properties. Example loading levels include about 0.05 $\mu g/cm^2$ to about 10 $\mu g/cm^2$, more preferably from about 0.1 $\mu g/cm^2$ to about 5 $\mu g/cm^2$ and more preferably from about 0.8 $\mu g/cm^2$ to about 3 $\mu g/cm^2$. These values depend strongly on the dimensions and spatial dispersion of the nanowires.

Typically, the optical transparence or clarity of the GMR nanowire sensor layer can be quantitatively defined by parameters including light transmission and haze. "Light transmission" refers to the percentage of an incident light transmitted through a medium. In various embodiments, the light transmission of the nanowire layer is between 50% and 98% (or any subrange there between). For a transparent sensor in which the nanowire layer is deposited or laminated on a substrate, the light transmission of the overall structure may be slightly diminished. Performance-enhancing layers, such as an adhesive layer, anti-reflective layer, anti-glare layer, may further contribute to reducing the overall light transmission of the transparent nanowire layer. In various embodiments, the light transmission of the transparent sensors can be at least 50%, at least 60%, at least 70%, or at least 80% and may be as high as at least 91% to 92%.

In certain embodiments, adhesion agents may be added to enhance the stability and/or promote the adhesion of the matrix and the GMR nanowires. For example, an adhesion promoter (e.g., silanes) that promotes the coupling between organic matter and inorganic matter can be used. Examples of the silane-type adhesion promoters include GE Silquest A174, GE Silquest A1100 and the like. Antioxidants such as Ciba Irgonox 1010ff, Ciba Irgonox 245, Irgonox 1035 can be used.

The GMR nanowire sensor layer may be formed by application of the carrier solution to the substrate by any number of convention or future developed application techniques. Printing technologies are sometimes divided between "sheet-based" and "roll-to-roll-based" approaches. Sheet-based techniques, such as inkjet and screen printing are best for low-volume, high-precision work. Gravure, offset and flexographic printing are more common for high-volume production, Thus, application techniques may include sheet coating, high throughput web coating, laminating, spray coating, ink jet printer application, ink pen application, metering rod application, micro-contact printing, vacuum filtration, roll-to-roll application, line patterning or an airbrush technique. In particular, the carrier solution may be applied by any printed electronics technique.

Printed electronics techniques are a set of printing methods used to create electrical devices on various substrates. Printing typically uses common printing equipment or other low-cost equipment suitable for defining patterns on material, such as screen printing, flexography, gravure, offset lithography and inkjet. Electrically functional electronic or optical inks are deposited on the substrate, creating active or passive devices, such as thin film transistors or resistors.

Typically, the fabrication processes can be carried out using conventional solution-processing equipment. Moreover, the fabrication processes are generally compatible with directly patterning the GMR nanowire layer. In the typical embodiment, the GMR nanowires being applied to a substrate in solution form results in the nanowires being positioned in a substantially random orientation when adhered to the substrate material. In other words, the nanowires will have a random orientation in the x-y plane parallel to the substrate. The SEM image of FIG. **15** showing a nanowire GMR thin film on PET substrate illustrates this random orientation. FIG. **15** also suggests how in many embodiments, the GMR nanowires will lie substantially flat on the substrate, generally parallel to the x-y plane of the substrate (e.g., oriented perpendicular to the z-axis).

As an example of sheetcoating, GMR nanowires dispersion may be initially deposited onto the substrate. A roller is rolled across a top surface of the substrate, leaving a nanowires dispersion layer on the substrate top surface. It is understood that a brush, a stamp, a spray applicator, a slot-die applicator or any other suitable applicator can be used in the place of the roller.

Web-coating has been employed in the textile and paper industries for high-speed (high-throughput) coating applications. It is compatible with the deposition (coating) processes for nanowire sensor fabrication. Advantageously, web-coating uses conventional equipment and can be fully automated, which dramatically reduces the cost of fabricating nanowire sensors. In particular, web-coating produces uniform and reproducible nanowire layers on flexible substrates. Naturally, any of the process steps described herein can be run on a fully integrated line or serially as separate operations.

In certain situations, the GMR nanowires may have the tendency to aggregate together into clumps and after time sedimentation of the nanowires occurs. To overcome this problem, ultrasonication of the GMR ink (carrier fluid) may be used to help disperse the GMR nanowires and other additives more uniformly. Example ultrasonication procedures include using an ultrasonication bath or an ultrasonication probe. During the ultrasonication process, the GMR nanowires may become fragmented (break apart) or bent (curved) depending on the amount of energy and time used during the ultrasonication process.

In certain embodiments, an annealing step may be applied to GMR nanowire networks in order to promote fusion of the nanowires leading to better electrical conductivity. The nanowires may be placed in a furnace between 50° C. and 250° C. for approximately 10-180 minutes in either an air or reducing atmosphere environment. The temperature and time of the annealing process depends on the diameter, length, and chemical makeup of the nanowires. In addition, the density of nanowires in the network, additives, and substrate will affect the annealing process. Care should be taken not to "melt" the multilayers of the GMR nanowires together, which may cause a significant decrease in the magnetoresistance property. Naturally, the substrate should be of a material capable of withstanding the annealing temperatures.

Returning to FIG. **1**, the position sensor **1** is formed by the magnetic field sensor **2** adhered to substrate **10** with conductors **7** and **8** ultimately connecting the magnetic field sensor **2** to a detection circuit (which is explained further below). It will be understood that as magnet **5** moves across a magnetic field sensor **2**, the resistance is lowered through the GMR nanowire layer **3** and such lowered resistance may be registered with the detection circuit. Obviously, the field of sensors **2** may be arranged in any particular configuration. For example, FIG. **4** illustrates how the position sensor may have a circular configuration with conductor **7** being a formed in two semi-circular segments. The embodiment of FIG. **4** suggests how the magnetic field sensor **2** can take shapes other than serpentine lines **3**. In FIG. **4**, magnetic field sensor **2** is a merely a circular or elliptically shaped layer of dried GMR nanowires which is in electrical contact with the conductors **7** and **8**.

In certain embodiments, the sensor has a resistance of at least about 0.5Ω/□ to 50 k Ω/□, where the "□" symbol represents unit area. In other embodiments, the sensor may be characterized as having a resistance change of at least about 0.01% per mT to 5% per mT (i.e., milli-Teslas). Typically, higher sensor sensitivity is achieved using some type of flux concentrator as described in more detail below. Certain sensor embodiments may have a magnetic saturation point of around 600 mT. These sensors have a 1.6% hysteresis error for a unipolar hysteresis test and a 9.1% hysteresis error for a bipolar hysteresis test.

A further example of a two-dimensional position sensor is seen in FIG. **10**. In this embodiment, a coversheet **15** with a series of indicia (images of different fruits in this illustration) is formed of some suitable thin nonconductive, nonmagnetic material. The coversheet **15** is then position on/over substrate **10** which has a series of magnetic field sensors **2** formed thereon in a two dimensional array. Although not explicitly show in FIG. **10**, it will be understood that conductors will be attached to each of the sensors **2** and such conductors will be attached to a detection circuit. It can be seen how one or more of the magnetic field sensors **2** will be positioned under each indicia **16**. Thus, when a magnet is placed over an indicia, at least one sensor **2** will experience a change in resistance. In the particular embodiment of FIG. **10**, a ferrous material sheet **17** is positioned behind substrate **10** and will provide a means for allowing a magnet to magnetically adhere to the surface of the position sensor. It will be readily understood that a user (e.g., a shopper in a grocery store) wishing to indicate a particular fruit (e.g., at an automated price checker) will simply move a magnet over the particular fruit indicia desired. Although FIG. **10** suggests a flat two dimensional array, it may be envisioned that a flexible planar substrate could be applied to a curved surface, which should still be considered a two dimensional array for purposes of this disclosure. Nevertheless, those skilled in the art will recognize techniques for employing the concepts described herein in three dimensional configurations.

As referenced above, the illustrated position sensor embodiments will typically employ a detection circuit to identify when a magnetic field sensor **2** has encountered a change in magnetic field strength. One embodiment of such a detection circuit is seen in FIG. **12**. This detection circuit **24** illustrates a substrate **10** with an array **35** of magnetic sensors **2** (in this example, serpentine line magnetic field sensors **3**) positioned on the substrate **10**. An output voltage is formed from a voltage divider created by a magnetic field sensor **30** and a magnetic sensor **2** located in the array **35**. A resistance change from each magnetic sensor in array **35** can be identified by using this detection circuit. One of the nine sensors **2** in array **35** may be selected to form a voltage divider with sensor **30** using multiplexers **25**. Multiplexer **25*a*** connects the sensor rows in array **35** to analog-to-digital converter **27** and sensor **30**. Sensor **30** terminates in voltage source **26**. Multiplexer **25*b*** connects the column of sensors in array **35** to ground **29**. An output voltage is created between sensor **30** and one of the nine sensors **2** located in array **35**. Conductors **7** from individual sensors **3** will terminate in a first multiplexer **25*a*** while conductors **8** will terminate in a second multiplexer **25*b***. The microprocessor **28** connects the correct multiplexers channel to the multiplexers' input. An analog-to-digital converter **27** is positioned within the circuit in order to convert the voltage from the voltage divider into a digital value to be communicated to the microprocessor. Naturally those skilled in the art will recognize that circuit **24** is just one possible detection circuit and many alternative conventional and future developed detection circuits could be employed.

FIG. **5** illustrates an alternative position sensor arrangement. In this embodiment, "push button" magnets **50** are positioned over one or more of the magnetic field sensors **2**. When the magnets are depressed, they move closer to the magnetic field sensors and reduce the resistance across the GMR nanowire serpentine line segments **3**. This allows a detection circuit to distinguish which of a plurality of push button magnets **50** has been activated by a user. FIGS. **6**A and **6**B illustrate one example of a push button magnet structure **50**. This structure generally includes the housing **52**, the button **51** capable of moving upward and downward in housing **52**, an upper magnet **55**, a GMR nanowire sensor layer **3**, and a lower magnet **56**. A biasing mechanism will typically bias the magnet **55** away from GMR nanowire sensor layer **3**. In FIGS. **6**A and **6**B, the biasing mechanism is formed by magnets **55** and **56** being positioned in opposing polar orientation, thereby having tendency to repel one another. When button **51** is depressed, magnet **55** moves closer to GMR nanowire sensor layer **3** and changes the resistance across the sensor layer **3**. When the downward force on button **51** is removed, the opposing magnetic forces returns button **51** to its raised position. It will be understood that while magnet **56** affects the resistance of GMR nanowire sensor layer **3**, nevertheless, the movement of magnet **55** closer to sensor layer **3** causes a further measurable change in resistance. FIGS. **7**A and **7**B illustrate a similar push button apparatus, but with a slightly different biasing mechanism. In this embodiment, the spring **58** is used to bias upper magnet **55** away from GMR nanowire sensor layer **3**, thus eliminating the lower magnet **56** seen in FIGS. **6**A and **6**B.

FIGS. **8**A and **8**B illustrate a still further embodiment of a push button assembly. In FIG. **8**A, a cylindrical housing **52** has a flexible diaphragm **60** formed across its top, with the button **51** attached to diaphragm **60**'s top side and magnet **55** attached to its bottom side. Housing **52** is shown positioned over a GMR nanowire sensor layer **3**. The diaphragm **60** may be formed of any suitable elastic material allowing depression of button **51** to move magnet **55** downward as seen in FIG. **8**B and return magnet **55** to its upward position when the depressing force is removed. As described above, the pressing of button **51** is detected when the resistance across GMR nanowire sensor layer **3** is changed by the movement of magnet **55** closer to the sensor layer **3**. As one example, this push button assembly could form the buttons described above in reference to FIG. **5**. It will be understood that that additional layers of material could be added to many of the above embodiments. For example, a non-magnetic material layer can be between the magnets and sensors for FIGS. **1**, **4**, **5** in order to protect the sensors or for aesthetic purposes.

In another embodiment, a magnetic potentiometer could be fabricated by a three-terminal resistor structure with a sliding magnet which forms an adjustable voltage divider as in FIGS. **9**A to **9**C. First resister **86** and second resister **87** are created from serpentine lines of solidified GMR carrier solution. Both first resister **86** and second resister **87** are connected to output terminal **89** while first resister **86** is also connected to voltage source **88**. It can be understood that as magnet **90** changes its position relative to first resister **86** and second resister **87**, the respective resistance of those resisters also changes. This creates the voltage divider effect, causing the voltage at output **89** to change with respect to the position of magnet **90**.

FIG. **11** suggests a still further component used in different embodiments of the present invention. In FIG. **11**, a carrier material **75** (e.g., a paper roll) is shown with a series of removable magnetic field sensors **2** positioned thereon. The magnetic field sensors **2** will comprise an adhesive substrate material **70** (e.g., a paper "sticker" segment with an adhesive material holding it to carrier material **75**) where the GMR nanowire sensor serpentine layer **3** is formed on the adhesive substrate material. It can be visualized how these magnetic field sensors **2** may be removed from carrier material **75** and adhered to another base to form any type of sensor, including an array of sensors such shown in previous figures or otherwise. It will be understood that conductors **7** and **8** and other elements of a detection circuit seen in FIG. **12** will be connected to the array of sensors to create the desired configuration of position sensor.

One modification to the above sensors could be the use of Wheatstone bridges. GMR materials themselves are very temperature dependent; however, simple arrangements, such as Wheatstone bridge circuits, can be applied to eliminate the temperature dependence. Many commercial GMR sensors are configured in the Wheatstone bridge configuration to decrease the temperature dependence, reduce noise, and as well create a linear output for the sensor. A Wheatstone bridge configuration with two active GMR resistors and two shielded GMR resistors could be used to eliminate temperature dependence and create a linear output. The resisters in the Wheatstone bridge circuit may be formed from serpentine lines of solidified GMR carrier fluid similar to the resister structures seen in FIG. **9**A. Of course, in none of the disclosed embodiments do the resisters need to be formed of serpentine lines, rather the resisters could be formed by virtually any layer (regardless of shape) of solidified GMR carrier fluid.

While the above embodiments have been described in terms of position sensors, many other types of devices could employ a similar type of GMR nanowire sensor layer. For example, magnetometers used to measure the strength or direction of a magnetic field and output a signal accordingly. A gradiometer may be used to detect magnetic field gradients found between GMR resistors in a Wheatstone bridge configuration. Unlike the magnetometer, gradiometer devices are unshielded allowing all four resistors in the Wheatstone bridge to be active. The gradiometer output can be bipolar versus unipolar and can be shaped by the use of a biasing magnet or flux guides.

The maximum current density carried by the GMR nano wire solidified layer typically depends on the loading density of the nanowires in the layer. Typically, the current through the nanowire layer will be less than 500 mA, and more preferably less than 100 mA, less than 50 mA, less than 10 mA, less than 1 mA, less than 0.5 mA, or less than 0.1 mA.

FIG. **13** illustrates another embodiment where the magnetic sensors may be used for ferromagnetic (metal) object detection. Normally when no ferromagnetic object **65** is present close to the sensor **2**, the magnetic field surrounding the sensor comes from a biasing magnetic field. The biasing magnetic field can come from any source **66** that produces a magnetic field, including permanent magnets, electromagnets, and the earth magnetic field. When a ferromagnetic object **65** comes into vicinity of the magnetic sensor **2**, the magnetic field around the sensor is distorted and the change in the magnetic field can be detected by the sensor.

In order to enhance the sensitivity of magnetic sensors, flux concentrators, can be used to concentrate the magnetic field in the preferred direction across the magnetic sensors to achieve the desired amount of sensitivity. FIG. **14** suggests one embodiment of a flux concentrator structure **80**. Elongated pieces of soft magnetic material **81** gather external magnetic flux and expose the sensor **2** to a magnetic field that is larger than the external magnetic field. Preferably, two pieces of soft magnetic material **81** of the same size are employed. The concentration factor is approximately the ratio of one flux concentrator's length to the gap between the two flux concentrators. The long dimension of the flux concentrators should butt up against the sensor structure. One example of a suitable soft magnetic material for use in the flux concentrators is a permalloy. By employing flux concentrators, the sensitivity of magnetic sensors can be increased by a factor of 2 to 100.

Although the present invention has been described in terms of specific embodiments, those skilled in the art will recognize many variations and modifications of those embodiments. For example, while most the above described embodiments deal with GMR nanowires, other nanowire types, e.g., TMR nanowires, CMR nanowires AMR nanowires, or OMR nanowires could potentially be used in alternative embodiments. All such variations and modifications are intended to come within the scope of the following claims.

The invention claimed is:

1. A magnetic position sensor comprising:
a. at least one magnetic field sensor comprising a solidified layer of GMR nanowire carrier fluid formed on a substrate material, wherein the solidified layer of carrier fluid comprises:
  i. discrete GMR nanowires each having a diameter of less than about 0.5 μm and a length less than about 250 μm; and
  ii. a concentration of GMR nanowires in the solidified layer being between about 0.001 and about 10 percent by weight of the carrier fluid;
b. a detection circuit capable of detecting a change in resistance of the magnetic field sensor; and
c. a magnet allowing relative movement closer to or further away from, the magnetic field sensor.

2. The magnetic position sensor of claim **1**, wherein the magnetic field sensor and the magnet are positioned in a housing and a biasing mechanism urges the magnet and magnetic field sensor apart.

3. The magnetic position sensor of claim **1**, further comprising a plurality of magnetic field sensors positioned on the substrate in a two dimensional configuration.

4. The magnetic position sensor of claim **3**, wherein a plurality of indicia are positioned over the substrate such that each indicia corresponds to at least one magnetic field sensor, thereby causing a change in resistance in the at least one magnetic field sensor as the magnet is moved over the indicia.

5. The magnetic position sensor of claim **1**, wherein the solidified layer of carrier fluid has at least about 100 nanowires per mm^2.

6. The magnetic position sensor of claim **1**, wherein the GMR nanowires are positioned in a substantially random orientation when adhered to the substrate material.

7. The magnetic position sensor of claim **1**, further comprising a corrosion inhibitor which is at least one of a barrier-forming corrosion inhibitor or a scavenger corrosion inhibitor.

8. A GMR material carrying solution comprising:
a. a carrier fluid;
b. a concentration of discrete GMR nanowires contained in the carrier fluid, wherein:
i. the discrete GMR nanowires each having a diameter of less than about 0.5 μm and a length less than about 200 μm;
ii. the GMR nanowires have an aspect ratio of at least five;
iii. the concentration of GMR nanowires being between about 0.005 and about 10 percent by weight of the carrier fluid.

9. The GMR material carrying solution according to claim **8**, wherein the carrier fluid comprises
0.0001% to 0.5% of a surfactant;
0.01% to 15% of a viscosity modifier; and
80% to 99.0% of a solvent.

10. The GMR material carrying solution according to claim **8**, wherein the carrying solution comprises at least one solvent selected from group consisting of water, an alcohol, a ketone, an ether, a hydrocarbon or an aromatic solvent.

11. The GMR material carrying solution according to claim **8**, wherein the carrying solution comprises at least one of a dispersion agent, a viscosity control agent, a corrosion inhibitor, or an adhesion agent.

12. The GMR material carrying solution according to claim **8**, wherein the discrete nanowires each have a diameter of less than about 0.2 μm and a length less than about 100 μm.

13. The GMR material carrying solution according to claim **8**, wherein GMR nanowires comprise alternating ferromagnetic and non-magnetic conductive layers.

14. The GMR material carrying solution according to claim **8**, wherein the carrier fluid includes an ink, dye, or other pigment.

15. The GMR material carrying solution according to claim **8**, wherein the carrier fluid is substantially transparent.

16. The GMR material carrying solution according to claim **8**, further comprising a flux concentrator agent.

17. The GMR material carrying solution according to claim **8**, further comprising a corrosion inhibitor.

18. A method of forming a magnetic field sensor comprising the step of adhering a solidified layer of GMR nanowire carrier fluid to a substrate material, wherein the GMR nanowire carrier fluid comprises:

i. discrete GMR nanowires in the carrier fluid each having a diameter of less than about 0.5 μm and a length less than about 200 μm; and

ii. a concentration of GMR nanowires in the carrier fluid being between about 0.01 and about 10 percent by weight of the solution;

iii. wherein the GMR nanowires are positioned in a random orientation when adhered to the substrate material.

19. The method of forming a magnetic field sensor according to claim **18**, wherein the GMR nanowire carrier fluid is adhered to the substrate by drying the carrier fluid on the substrate.

20. The method of forming a magnetic field sensor according to claim **18**, wherein the substrate is a flexible sheet of polymer material.

21. The method of forming a magnetic field sensor according to claim **18**, wherein the carrier fluid is applied to the substrate using at least one sheet based or roll-to-roll based printing techniques.

22. The method of forming a magnetic field sensor according to claim **18**, wherein the sensor has a resistance change of about at least 0.01% per mT.

23. The method of forming a magnetic field sensor according to claim **18**, wherein the sensor is formed in a predefined shape on the substrate by applying the carrier fluid to a stamp having the predefined shape and then applying the stamp to the substrate in order transfer the carrier fluid to the substrate.

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