



MAGNETICALLY-ANNEALED NANOWIRES AND METHODS OF FABRICATING THE SAME

5 FIELD OF THE INVENTION

The present invention relates to magnetically-annealed nanowires and methods of fabricating the same. In particular, but not exclusively, the present invention relates to magnetic films formed with magnetically-annealed nanowires and methods of
10 fabricating the same.

BACKGROUND TO THE INVENTION

A typical magnet provides a magnetic field in a particular volume of space. In contrast
15 to traditional bulk magnets, thin magnetic films are being used in microdevices in which a magnetic field is required within a confined space (micrometer range) for the working mechanism of the devices.

Recently, magnetic films in the form of magnetic nanowires have been developed as a
20 permanent magnetic film for such applications. The nanowires may be provided in an array form and may be embedded in a matrix. An example form of nanowires embedded in a matrix is described in an article entitled 'Effect of Magnetic Field Annealing Upon Co-Rich Nanowires' by Sharif et al, which was published in Volume 42 of the IEEE Transactions on Magnetism.

25



It is an object of the present invention to either provide nanowires with improved hard magnetic properties, or at least provide the public with a useful choice.

SUMMARY OF THE INVENTION

5

In general terms, in a first aspect, the present invention relates to a method of magnetically annealing nanowires, with an average diameter of 60nm or less. This may have the advantage that a substantial deterioration in remnant magnetisation (B_r) during annealing is avoided.

10

In general terms, in a second independent aspect, the present invention relates to magnetically-annealed nanowires, with an average diameter of 60nm or less. This may have the advantage that the remnant magnetisation (B_r) is improved.

15 In a first specific expression of the invention, there is provided a method comprising: providing a plurality of nanowires, with an average diameter of 60nm or less and being arranged substantially parallel to each other along their longitudinal axis, annealing the nanowires, and applying a magnetic field that is aligned with the longitudinal axis of the nanowires at least partially during annealing.

20

In a second specific expression of the invention, there is provided a magnetic film comprising an array of magnetically-annealed nanowires, with an average diameter of 60nm or less and being arranged substantially parallel to each other along their longitudinal axis.

As used herein, the terms 'comprising' and 'comprises' mean 'consisting at least in part of', that is to say, when interpreting statements in this specification and claims that include those terms, the features prefaced by the terms in each statement all need to be
5 present but other features can also be present.

The present invention may also be said broadly to consist in the parts, elements and features referred to or indicated in the specification, individually or collectively, and any or all combinations of any two or more said parts, elements or features, and where
10 specific integers are mentioned herein which have known equivalents in the art to which this invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

BRIEF DESCRIPTION OF THE FIGURES

15

Example embodiments will now be described with reference to the accompanying figures in which:

20

Figure 1 is an example graph of magnetisation (M) versus applied magnetic field (H).

Figure 2 is a flowchart of a method of fabricating magnetically-annealed nanowires according to an exemplary embodiment.

Figure 3 is a perspective view of an array of nanowires embedded in a matrix.

Figure 4A is a perspective view of a magnetic field that is aligned with the longitudinal axis of the array of Figure 3.

- 5 Figure 4B is a perspective view of the resulting array of magnetically-annealed nanowires from Figure 4A.

Figure 5 is an image of a bundle of nanowires with an average diameter of about 350-400nm.

10

Figure 6 is an image of nanowires with an average diameter of around 65-70nm embedded in a matrix.

15

Figure 7 is an image of a single nanowire with an average diameter of around 45-50nm.

Figure 8 is an M-H curve of nanowires with an average diameter of around 350-400nm.

Figure 9 is an M-H curve of nanowires with an average diameter of around 65-70nm.

- 20 Figure 10 is an M-H curve of nanowires with an average diameter of around 45-50nm.

DETAILED DESCRIPTION OF EXAMPLE EMBODIMENTS

The performance of a magnet can be assessed by a hysteresis curve. An example
5 hysteresis curve for a plurality of nanowires shown in Figure 1, measured parallel to the
longitudinal axis of the nanowires. Two magnetic characteristics that can be extracted
from the curve are coercivity (H_c) and remnant magnetisation (B_r). A high H_c indicates
that the magnet will not be demagnetised easily. A high B_r indicates a high magnetic
field strength will be deliverable by the same volume of magnet. Hence, a high
10 performance permanent magnet should ideally have a high H_c and high B_r . The
applicant has identified that both H_c and B_r of magnetic nanowires are dependent on the
choice of materials, fabrication and post-fabrication processing.

As used herein, the term 'magnetically-annealed' in relation to nanowires refers to
15 nanowires that have been annealed at least partially in the presence of an applied
magnetic field that is aligned with the longitudinal axis of the nanowires. Similarly, the
term 'magnetic annealing' in relation to nanowires refers to the process of annealing
nanowires at least partially in the presence of an applied magnetic field that is aligned
with the longitudinal axis of the nanowires.

20

A method of fabrication 20 according to an exemplary embodiment is illustrated in
Figure 2. In step 22, a plurality of nanowires is provided. The nanowires have an
average diameter of 60nm or less and are arranged substantially parallel to each other
along their longitudinal axis. In step 24, the nanowires are annealed. In step 26, a

magnetic field is applied to the nanowires, aligned with the longitudinal axis of the nanowires, at least partially during annealing.

The nanowires are composed of an alloy including cobalt and iron (CoFe), for example
5 a composition of Co_xFe_y , where x is 45-55, y is 45-55. Other compositions may be used incorporating, for example, one or more of iron, nickel, cobalt and silicon, depending on the requirements of the application.

Providing the nanowires 22 may be implemented by depositing the nanowires within
10 pores of a matrix 32, forming a nanowire array 36, as shown in Figure 3. The nanowires have an average diameter less than 60nm. For example, the average diameter may be less than 55nm or less than 50nm. For instance, the diameter may be between 40-60nm or between 45-50nm. In one embodiment, the nanowires have an average diameter of 50nm. In another embodiment, there is no significant portion (e.g. greater
15 than 5%) of nanowires having a diameter above 60nm. In the latter embodiment, the nanowires may be provided as a subset of a larger group of nanowires that may have an average diameter outside of the above range.

The nanowires 30 may have a cylindrical shape with a high aspect ratio i.e. large
20 vertical height to small lateral diameter. This may provide the nanowires 30 with shape anisotropy, which, in turn, provides better magnetic properties (e.g. high coercivity). With such properties, the nanowires 30 can be used as a permanent magnet or magnetic film with a magnetic axis along the longitudinal axis of the nanowires, shown generally with reference numeral 34.

The matrix 32 is, for example, an anodised aluminium oxide (AAO) matrix. By using an AAO matrix, the nanowires may be formed cost-effectively using an electrodeposition process. For instance, where the nanowires should have a composition of cobalt-iron (CoFe), and the matrix is an AAO matrix, the nanowires may be electrodeposited by first sputtering one side of the AAO with an electrically-conductive material to provide a seed layer. For instance, a 200nm-thick gold layer may be sputtered. Alternatively, silver or copper could be used instead. Electrodeposition is carried out using a rotating disk electrode system via a galvanostat/potentiostat. Silver potassium chloride (Ag/KCl) is used as the reference electrode while a pure platinum wire is used as the anode. An example composition of the electrolyte solution for electroplating CoFe within the pores of the AAO template is given in Table 1. Electroplating conditions of current density and agitation speed are also given in Table 1. In consideration of the overall plating area inclusive of the anodised aluminium oxide regions, current density is about 0.53 A/cm^2 .

Electrochemical Bath Composition	Concentration (CoFe)
B(OH) ₃	0.6 mol/L
CoSO ₄ .7H ₂ O	0.125 mol/L
FeSO ₄ .H ₂ O	0.095 mol/L
Current Setting	0.15A
Plated anodized aluminium oxide area	6mm diameter circle
Agitation (Rotation) Speed	250 rpm

Bath Temperature	Room Temperature
Natural Bath pH	3.7

Table 1: Summary of Electrolyte Composition & Electroplating Conditions

During electroplating using the above-specified parameters, CoFe nanowires would
5 grow from the bottom of the pores (i.e. from the seed layer) and along the channels of
the pores of the AAO matrix. As a result, arrays of CoFe nanowires would be
fabricated and embedded within the pores of the AAO matrix. Using this process,
nanowires of different diameters can be fabricated by controlling the size of the pores of
the AAO matrix.

10 The applicant has found that as-deposited nanowires exhibit a relatively low H_c , which
stems from a low degree of crystallinity, high internal stress and defects in the
microstructure of the nanowires. To improve the H_c , the nanowires are annealed, which
is a form of thermal treatment to effect changes in the microstructure of materials.

15 Annealing the nanowires 24 may be implemented by exposing the array 36 to a relative
vacuum and at a temperature of between 100°C and 500°C. For instance, the nanowires
may be annealed at a temperature of 500°C. Also, the annealing process may be carried
out for between 1 hour and 5 hours. For instance, the nanowires may be annealed for a
20 duration of 2 hours. Different temperature and duration values may be used instead of
those described above, and one or more cycles of annealing may be carried out,
depending on the application and/or desired characteristics.

Applying a magnetic field 26 may be implemented as shown in Figure 4A. The applied magnetic field 44 is aligned with the longitudinal axis of the nanowires 40. The magnetically-annealed nanowires 46 produced are shown in Figure 4B. In the form shown, the matrix 42 has been removed following annealing and application of the magnetic field. In an alternative form, the nanowires may have been originally provided without the matrix, in which case there is no matrix to remove to produce the array of magnetically-annealed nanowires 46 of Figure 4B.

10 The magnetic field applied to the nanowires may have a density of between 1T and 2T. For instance, the magnetic field may have a density of 1T. As with the temperature and duration of annealing, the density of the magnetic field may be changed to suit specific needs or desires. A change in any of the above parameters may affect the structure and magnetic properties of the nanowires, and so the parameters may be altered to suit the
15 eventual application of the nanowires. Typically the magnetic field is applied at the same time as annealing the nanowires. The application of the magnetic field starts when the annealing process starts, and ends when the annealing process ends. Depending on the application the start and/or end of the application of the magnetic field may be at different times to the start and/or end of annealing, as long as the
20 application of the magnetic field is applied at least partially during annealing.

The annealing of nanowires with an average diameter of 60nm or less in the manner described above may prevent any substantial deterioration of remnant magnetisation (B_r) during annealing. The B_r after magnetic annealing may be improved. For instance,

the B_r after magnetic annealing may be between 1 % and 25 % higher, between 1% and 5% higher, or at least 3% higher than the value before magnetic annealing.

For clarification, an example will be described below with reference to an experiment
5 and its results. The conditions and materials described in the experiment are example parameters and are not essential.

In the experiment, three different types of CoFe nanowires with different diameters, namely 350-400nm, 65-70nm and 45-50nm, were grown using the electrodeposition
10 process described earlier. The different diameter nanowires are shown respectively in the scanning electron microscopic (SEM) images of Figures 5, 6 and 7. Figure 6 shows a regular pattern of uniformly distributed nanowires embedded in an AAO matrix, while Figure 5 and 7 show nanowires that have been removed from the AAO matrix.

Removal, in the experiment, was done by wet-chemical-etching the nanowire array in
15 sodium hydroxide solution having a concentration of 1M for around 6 hours after electrodeposition of the nanowires.

One batch of each of the 350-400nm, 65-70nm and 45-50nm nanowires was subjected to annealing without application of a magnetic field during the annealing process. One
20 batch of the 45-50nm nanowires was subjected to annealing and an application of a magnetic field that was aligned with the longitudinal axis of the nanowires. The density of the magnetic field was 1T. For all batches, annealing was carried out in a vacuum environment at 500°C for 2 hours.

Magnetic hysteresis was measured in a direction parallel to the nanowires, before and after annealing, for all four batches (350-400nm, 65-70nm, 45-50nm and 45-50nm with magnetic field application). The resulting magnetic properties are tabled in Table 2 below and the resulting hysteresis graphs are shown in Figures 8 to 10. The term 'normal' in relation to annealed in Table 2 refers to annealing that is carried out without any application of a magnetic field.

Sample	Annealing	Before Annealing		After Annealing	
Size (nm)	Condition	B _r (kG)	H _c (kOe)	B _r (kG)	H _c (kOe)
350-400	Normal	0.14	0.1	1.55	0.4
65-70	Normal	6.58	1.9	7.77	2.3
45-50	Normal	6.23	2.3	4.79	2.8
45-50	Magnetic	6.23	2.3	6.43	2.8

Table 2: Results of Annealing Different-Diameter Nanowires

As can be observed in Table 2 and Figures 8-10, the H_c of the as-deposited nanowires with an average diameter of 350-400nm is rather low, and that H_c does not improve by much after normal annealing. A higher H_c was measured for the as-deposited nanowires with an average diameter of 65-70nm, and that H_c was further improved after normal annealing. A still higher H_c was measured for the as-deposited nanowires with an average diameter of 45-50nm, and that H_c was also further improved after normal annealing. It is therefore evident that coercivity (H_c) of the nanowires may be improved by designing the nanowires to have an average diameter of 60nm or less. Since a high

H_c indicates hard magnetic properties, it may be beneficial to form the nanowires with such a diameter and to further improve the H_c by annealing.

The results in Table 2 also show the change in B_r after annealing. For nanowires with an average diameter in the range of 350-400nm or 65-70nm, the B_r improves after normal annealing. For nanowires with an average diameter in the range of 45-50nm, however, the B_r may deteriorates significantly after normal annealing, dropping from 6.23 kG to 4.79 kG. This can be contrasted with the results of magnetically-annealed nanowires having a similar diameter. As can be seen in Table 2 and in Figure 10, the magnetically-annealed nanowires may suffer no deterioration and, in fact, may have an improved B_r , for example increasing from 6.23 kG to 6.43 kG (an improvement of around 3.2%).

As the above results indicate, deterioration in B_r of nanowires having an average diameter of 60nm or less, can be avoided during annealing. Any such prevention in B_r deterioration would improve the potential of the nanowires in, for example, applications in magnetic microdevices as a thin permanent magnetic film.

Besides the embodiment relating to a method above, there is also disclosed an embodiment relating to an array of magnetically-annealed nanowires. A schematic of the array of magnetically-annealed nanowires is shown in Figure 4B and was described briefly earlier in this specification. As before, the nanowires in the array have an average diameter of 60nm or less and are arranged substantially parallel to each other along their longitudinal axis. Depending on the application the features and properties

of the nanowires noted earlier in relation to the method embodiment may also apply to this embodiment relating to the array of nanowires.

The foregoing describes exemplary embodiments, which, as will be understood by those skilled in the art, may be subject to many variations or modifications in design, construction or operation without departing from the scope of the present invention as claimed. For example, while the method embodiment has been described with reference to steps to be carried out in a certain order, the method may be modified such that the steps are carried out in a different order, where appropriate. Also, the method may be modified such that additional steps carried out. Such variations, for instance, are intended to be covered by the scope of the present invention as claimed.

CLAIMS

1. A method comprising:
 - providing a plurality of nanowires with an average diameter of 60nm or less
 - 5 and being arranged substantially parallel to each other along their longitudinal axis,
 - annealing the nanowires, and
 - applying a magnetic field that is aligned with the longitudinal axis of the
 - nanowires at least partially during annealing.
- 10 2. The method as claimed in claim 1 wherein the nanowires have an average diameter of 55nm or less.
3. The method as claimed in claim 1 wherein the nanowires have an average diameter of 50nm or less.
- 15 4. The method as claimed in claim 1 wherein the nanowires have a composition including cobalt and iron (CoFe).
5. The method as claimed in claim 4 wherein the nanowires have a composition of
- 20 Co_xFe_y , where x is 45-55, y is 45-55.
6. The method as claimed in any one of the preceding claims wherein providing the nanowires comprises embedding the nanowires in a matrix to form a nanowire array.

7. The method as claimed in claim 6 wherein the matrix is an anodised aluminium oxide (AAO) matrix.
- 5 8. The method as claimed in claim 7 wherein embedding the nanowires comprises electrodepositing a composition into a plurality of pores in the matrix.
9. The method as claimed in claim 8 wherein electrodepositing comprises:
sputtering one side of the AAO matrix with a layer of electrically-conductive
10 material, and
electroplating CoFe in the nanopores of the AAO matrix using a rotating disk electrode system having a silver potassium chloride (Ag-KCl) reference electrode, a pure platinum wire anode and an electrolyte solution comprising around 0.6 mol/L of boric acid (B(OH)_3), around 0.125 mol/L of cobalt sulphate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) and around
15 0.095 mol/L of ferrous sulphate ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$).
10. The method as claimed in any one of claims 1-9 wherein the nanowires have an average diameter of between 40nm and 60nm.
- 20 11. The method as claimed in claim 10 wherein the nanowires have an average diameter of 50nm.
12. The method as claimed in any one of claims 1 to 11 wherein annealing comprises applying an elevated temperature of between 100°C and 500°C to the nanowires.

13. The method as claimed in claim 12 wherein the elevated temperature is 500°C.
14. The method as claimed in any one of claims 1 to 12 wherein annealing comprises
5 applying an elevated temperature for a duration between 1 hour and 5 hours to the nanowires.
15. The method as claimed in claim 14 wherein the duration is 2 hours.
- 10 16. The method as claimed in any one of claims 1 to 15 wherein annealing further comprises applying an elevated temperature in a relative vacuum.
17. The method as claimed in any one of claims 1 to 16 wherein applying a magnetic field comprises applying a magnetic field having a density of between 1T and 2T.
- 15 18. The method as claimed in claim 17 wherein the density is 1T.
19. The method as claimed in any one of claims 1 to 18 wherein remnant magnetisation (B_r) of the nanowires is improved after magnetic annealing.
- 20 20. The method as claimed in claim 19 wherein the B_r of the nanowires after magnetic annealing is between 1% and 25% higher than the B_r before magnetic annealing.

21. The method as claimed in claim 20 wherein the B_r of the nanowires after magnetic annealing is between 1% and 5% higher than the B_r before magnetic annealing.
22. The method as claimed in claim 19 wherein the B_r of the nanowires after magnetic
5 annealing is at least 3% higher than the B_r before magnetic annealing.
23. The method as claimed in any one of claims 19 to 22 wherein the B_r is measured parallel to the longitudinal axis of the nanowires.
- 10 24. The method as claimed in any one of claims 1 to 23 wherein applying a magnetic field comprises applying a magnetic field at the same time as annealing the nanowires.
25. A magnetic film comprising a plurality of nanowires fabricated in accordance with the method as claimed in any one of the preceding claims.
- 15 26. A magnetic film comprising an array of magnetically-annealed nanowires having an average diameter of 60nm or less and being arranged substantially parallel to each other along their longitudinal axis.
- 20 27. The magnetic film as claimed in claim 26 wherein the nanowires have an average diameter of 55nm or less.
28. The magnetic film as claimed in claim 25 wherein the nanowires have an average diameter of 50nm or less.

29. The magnetic film as claimed in claim 26 wherein the nanowires have a ferroelectric composition including cobalt and iron (CoFe).
- 5 30. The magnetic film as claimed in claim 29 wherein the nanowires have a composition of Co_xFe_y , where x is 45-55, y is 45-55.
31. The magnetic film as claimed in any one of claims 26 to 30 further comprising a matrix in which the nanowires are embedded.
- 10 32. The magnetic film as claimed in claim 31 wherein the matrix is an anodised aluminium oxide (AAO) matrix.
33. The magnetic film as claimed in any one of claims 26 to 32 wherein the nanowires
- 15 have an average diameter of between 40nm and 60nm.
34. The magnetic film as claimed in claim 33 wherein the average diameter is 50nm.