Magnetic field alignment of template released ferromagnetic nanowires
Musaab S. Sultan, Bipul Das, Kalyan Mandal, and Del Atkinson

Citation: Journal of Applied Physics 112, 013910 (2012); doi: 10.1063/1.4730967
View online: http://dx.doi.org/10.1063/1.4730967
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/112/1?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Enhanced magnetic anisotropy of Ni nanowire arrays fabricated on nano-structured silicon templates

Electrochemical synthesis of highly ordered magnetic multilayered nanowire arrays

Magnetophoretic assembly and printing of nanowires
J. Vac. Sci. Technol. B 30, 021603 (2012); 10.1116/1.3683152

Magnetic properties of arrays of nanowires: Anisotropy, interactions, and reversal modes
J. Appl. Phys. 107, 09B504 (2010); 10.1063/1.3350905

Structure and magnetic properties of hexagonal arrays of ferromagnetic nanowires
Musaab S. Sultan, Bipul Das, Kalyan Mandal, and Del Atkinson

Department of Physics, Durham University, South Road, DH1 3LE Durham, United Kingdom
5 S N Bose National Centre for Basic Sciences, Salt Lake, Kolkata 700 098, India

(Received 23 March 2012; accepted 27 May 2012; published online 6 July 2012; publishers error corrected 12 July 2012)

A detailed investigation of magnetic field alignment of template released ferromagnetic nanowires has been undertaken. The distributions of magnetic field induced angular alignments of Ni0.8Fe0.2, Co, and Ni nanowires grown by electro-deposition and deposited onto substrates from a dilute suspension have been investigated as a function of magnetic field strengths up to ~1 kOe. The nominal diameter of the nanowires investigated is either ~200 nm (Ni0.8Fe0.2) or ~300 nm (Co and Ni). The percentage of nanowires aligned within 0°–10° and 0°–20° of the applied field axis is observed to increase rapidly with increasing field strength up to ~200 Oe, followed by a slower increase in alignment for the Ni0.8Fe0.2 and Ni wires and little improvement in alignment for the Co wires at higher fields. The proportion of aligned wires within 0°–20° is found to reach ~82% for Ni0.8Fe0.2, ~71% for Ni and only 53% for the Co nanowires using a magnetic field of 1 kOe.

The influence of wire length upon the efficacy of magnetic alignment is investigated using Ni0.8Fe0.2 and Ni nanowires; this showed that the fractional alignment improved for longer nanowires. © 2012 American Institute of Physics.[http://dx.doi.org/10.1063/1.4730967]

INTRODUCTION

Quasi-one dimensional structures such as nanowires, nanorods, and nanotubes have become the focus of extensive studies over the past two decades as they present the opportunity to explore the fundamental physical properties and have a range of potential applications including: electronic, spintronic, and optoelectronic technology, as well as logic circuits, chemical, and biological systems.

One important technique that has been widely used to create these structures is electrodeposition, due to its ease of use, rapid preparation and low cost. Moreover, using this technique single composition, alloys, and compositionally modulated layers can be prepared. Nanostructure formation typically involves template deposition, with templates made from alumina, mica, and track-etched polycarbonate membranes. A variety of nanostructures can be formed from nanodots to nanotubes with cylindrical nanowires most commonly prepared. In many studies, the as-deposited templated arrays of nanowires have been investigated, and this has produced significant insight into the physical behaviour of these nanowires.

More recently, isolated individual nanowires have been studied, and these studies present the opportunity to investigate the intrinsic behaviour of individual nanowires. Isolated nanowires are obtained by releasing the nanowires from the templates using a suitable chemical solution to dissolve the template without damaging the nanostructures. With the template removed, a dilute suspension of nanowires can be formed in a suitable carrier solvent. By evaporation of the solvent, isolated nanowires can be dispersed onto a suitable substrate for further investigations.

For scientific study and also for potential applications of these wires, the manipulation and alignment are the significant and demanding issues. Therefore, a variety of techniques have been utilised to manipulate and control electrodeposited nanowires suspended in a solvent including thermocapillary motion of nanowire suspensions in micro-channels, electrostatics, electric field, and magnetic field assisted alignment. Recently, magnetic field have been utilized by several researchers to control assembly and alignment of carbon nanotubes, semiconductor, conductive polymer nanowires, as well as metallic nanowires such as gold, bismuth, copper-tin, Pt, and ZnO (Ref. 38) capped with Ni ends by manually drop casting a dilute suspension containing these nanowires between two electrodes predefined on a specimen by lithographic techniques and using two permanent magnets.

These studies have been performed to investigate and analyse the motion of these wires in the suspension under the influence of an applied field and the effects of viscosity of the solvents on the motion. In addition, recent work demonstrated the use of magnetic alignment of electrodeposited ferromagnetic nanowires to create hierarchical structures. Again, permanent magnets were used, this time for sequential alignment of the nanowires onto either un-patterned or pre-patterned ferromagnetic electrodes on substrates. The effects of shape, separation distances and dimensions of these electrodes and the local magnetic field on the alignment process have also been examined.

The torque exerted upon a nanowire in a uniform magnetic field is determined by the vector product: \( m \times H \), where \( m \) is the magnetic moment and \( H \) is the applied field. The magnetic moment \( m \) depends upon the magnetization, length, and cross-sectional area of the nanowire. It is therefore, reasonable to expect that the process of magnetic alignment will depend upon the strength of the magnetic field, the
saturation magnetization, and the aspect ratio (length to the diameter) of the nanowires. The alignment process is also affected by the resistive drag of the suspension solvent, which is likely to influence the timescale of the alignment process, which can be of the order of milliseconds. A further effect that may warrant consideration in the process is thermal agitation of the suspended nanowires, this will act to misalign the nanowires. In the situation where the suspension solution is evaporated to leave the nanowires deposited on a substrate, the interaction of the nanowires with the evaporating solvent and the substrate may further affect the alignment process, although this is difficult to analyse.

The alignment process is also affected by the resistive drag of the suspension solvent, which is likely to influence the timescale of the alignment process, which can be of the order of milliseconds. A further effect that may warrant consideration in the process is thermal agitation of the suspended nanowires, this will act to misalign the nanowires. In the situation where the suspension solution is evaporated to leave the nanowires deposited on a substrate, the interaction of the nanowires with the evaporating solvent and the substrate may further affect the alignment process, although this is difficult to analyse.

The goal of the work presented here is to quantitatively investigate the details of magnetic field alignment of template released Ni$_{0.8}$Fe$_{0.2}$ (permalloy), Ni, and Co nanowires. Specifically, this work investigates the alignment of nanowires deposited onto oxidised silicon substrates as a function of the strength of the magnetic field, the effect of composition (saturation magnetization), and the aspect ratio of the nanowires upon the alignment process. This work also reports some additional observations resulting from the magnetic alignment experiments.

**EXPERIMENTAL PROCEDURE**

Electro-deposition was used to create $\sim$20 $\mu$m length permalloy (with a nominal composition of Ni$_{0.8}$Fe$_{0.2}$), Ni and Co nanowires in alumina templates. These wires were prepared in commercially available $\sim$60 $\mu$m thick alumina templates (Anodisc Whatman, Inc.) with a nominal pore diameter of $\sim$200 nm for permalloy nanowires and $\sim$300 nm for the Ni and Co nanowires. The fabrication process was carried out using an Autolab-30 potentiostat with a three-electrode arrangement. The reference electrode used was Ag/AgCl, which has a standard potential of $\sim$0.22 V, while a platinum electrode was used as a counter electrode. A $\sim$100 nm thick layer of gold (purity $\sim$99.99%) was deposited by sputtering onto one side of the templates to block the nanopores and to serve as a working electrode in the electrochemical cell. To prevent the deposition directly onto the backside of the gold layer, the gold film was covered with a strip of insulating tape.

Ni (or Co) nanowires were prepared using 0.57 M of NiSO$_4$ (or CoSO$_4$) and 31 g/l of H$_3$BO$_3$. In order to create Ni$_{0.8}$Fe$_{0.2}$, the electrochemical bath consisted of 1.3 M of NiSO$_4$ and 0.151 M of FeSO$_4$ along with boric acid. The pH of the solution was controlled to be $\sim$4. The deposition voltage applied between the counter and the working electrodes was fixed to $\sim$0.9 V following linear sweep voltammetry results. Further details of nanowires fabrications are presented elsewhere.

The nanowire filled templates were subdivided into small sections and placed in 2 M NaOH to dissolve the alumina templates for a time of $\sim$48 hours at room temperature. The nanowires were washed repeatedly with distilled water and then with isopropanol (IPA). The nanowires were deposited onto clean SiO$_2$ capped silicon substrates by drop casting 15 $\mu$l drops of the dilute suspension to cover an approximate area of $\sim$8 mm $\times$ 10 mm. The solvent was allowed to evaporate under normal atmospheric conditions, which typically took a few minutes. For magnetic alignment, the substrates were placed horizontally between the pole pieces of a small electromagnet. Calibration of the electromagnet indicated a range of magnetic field strengths up to $\sim$1 kOe. The uniformity of the magnetic field across the area of the nanowires deposition was found to vary $\sim$10%.

In order to assess and analyse the efficacy of the magnetic alignment process, a detailed series of scanning electron microscopy imaging and analysis was made on a number of samples prepared under different field strengths and nanowires compositions. Imaging and image analysis was performed using a high-resolution field emission scanning electron microscopy column on a FEI-Helios Nanolab dual beam FIB/SEM system with an electron beam energy of 10 keV. For each sample, more than five hundred individual nanowires

![FIG. 1. Examples of scanning electron micrographs of deposited NiFe nanowires under (a) no applied magnetic field, (b) moderate, and (c) high magnetic field applied during deposition process.](image-url)
were studied to determine the angular orientation of the nanowire with respect to the alignment field axis. The distribution of diameters and lengths for each nanowire composition was also determined from these measurements. EDX analysis was used to confirm the composition of the nanowires.

RESULTS AND DISCUSSIONS

The influence of the magnetic field upon the alignment of Ni\textsubscript{0.8}Fe\textsubscript{0.2} nanowires is demonstrated in the electron microscopy micrographs shown in Figure 1. In the absence of applied field, the wires are randomly oriented as demonstrated in Figure 1(a). The random orientation of these wires can be attributed to various mechanical forces in the droplet of the suspension including fluid drag force and Brownian motion as well as the weight of the nanowires and buoyancy forces.\textsuperscript{34} Deposition with a moderate strength of applied field, the nanowires show modest alignment as demonstrated in Figure 1(b), whereas a more strongly aligned assemblage of nanowires occurs at the highest field investigated here (1 kOe), see Figure 1(c).

In order to quantitatively investigate the effect of magnetic field strength on the alignment process, a detailed statistical analysis was undertaken to determine the orientation angles of Ni\textsubscript{0.8}Fe\textsubscript{0.2}, Co, and Ni nanowires deposited at different field strengths up to \(\sim 1\) kOe.

Figure 2 shows the angular distribution histograms for assemblages of NiFe nanowires deposited at a range of magnetic field strengths. These wires have a nominal diameter of \(\sim 200\) nm and a broad distribution of lengths centred around \(\sim 10\) \(\mu\)m. In the absence of applied magnetic field, there is no preferred orientation in the assemblage of nanowires (see Figure 2(a)). With increasing field up to \(\sim 200\) Oe, the distribution of nanowire orientation develops with respect to the field axis (Figures 2(b) and 2(c)), indicating the effect of the field. At higher fields \(\sim 500, 750,\) and \(1\) kOe, a strong peak in the distribution develops along the axis of the magnetic field as shown in Figures 2(d)–2(f).

The angular distribution of nanowires for field-aligned assemblages is not Gaussian, but it is characterised by a large number of nanowires oriented very close to the applied field axis surrounded by a distribution of nanowires over a wide range of angles.

![Angular distribution histograms for assemblages of NiFe nanowires deposited at different field strengths (0–1 kOe) as indicated in the figure titles.](image_url)
range of angles. The field alignment behaviour for NiFe nanowires is summarised in Figure 3, which shows the proportion of nanowires aligned at angles between 0°–10° and 0°–20° of the applied field axis as a function of magnetic field.

It is clear that, the percentage of NiFe nanowires aligned by the field increases rapidly up to ~200 Oe, then increases more slowly at higher fields up to the maximum field, when ~64% of the nanowires are aligned within 0°–10° and a total of ~82% of the nanowires are aligned within 0°–20° of the applied field axis. The high field dependence of the alignment suggests an approach to a maximum alignment with field, indicating that some further improvement in the proportion of aligned nanowires may be possible with magnetic fields >1 kOe.

Figure 4 shows a comparison of the angular distributions histograms for assemblages of Co and Ni nanowires deposited on the substrates at different field strengths. These wires have a nominal diameter of ~300 nm and a range of lengths centred around ~10 μm. For all field strengths investigated here, the percentage of aligned Ni wires is higher than for Co wires. Furthermore, the Ni wires show the emergence of clear alignment at a relatively low field of ~100 Oe compared to the Co nanowires, where similar alignment was not observed until the field was greater than ~180 Oe. The field alignment behaviour for Co and Ni nanowires is summarised in Figures 5(a) and 5(b), respectively, which shows the

FIG. 3. Proportion of NiFe nanowires aligned at angles between 0°–10° and 0°–20° as a function of the magnetic field strength applied during deposition process. The dashed lines are used as a guide to the eye.

FIG. 4. Comparison of angular distribution histograms for assemblages of 300 nm Co and Ni nanowires deposited at different field strengths (100–1 k) Oe as indicated in the figure titles.
proportion of nanowires aligned at angles between $0^\circ - 10^\circ$ and $0^\circ - 20^\circ$ of the applied field axis.

In general, the percentage of Ni nanowires aligned with the field increases rapidly with applied field up to $\sim 200$ Oe, then the percentage of aligned wires increases more slowly as magnetic field increases up to a maximum field, where $\sim 59\%$ of the wires are aligned within $0^\circ - 10^\circ$ and a total of $\sim 71\%$ within $0^\circ - 20^\circ$. The high field dependence of the alignment (see Figure 5(b)) indicates an approximately linear increase in the proportion of nanowires aligned as a function of magnetic field. Again, this suggests further improvements in the proportion of aligned Ni nanowires is possible with magnetic fields $> 1$ kOe. In contrast, the assemblages of Co nanowires show significant alignment at low fields, but the proportion of aligned nanowires at higher field strengths seems to saturate when the fractional alignment is $\sim 36\%$ aligned within $0^\circ - 10^\circ$ and a total of $\sim 53\%$ between $0^\circ$ and $20^\circ$ of the applied field axis.

The above results suggest that the nanowires react strongly to the magnetic field and as introduced earlier, that the magnetic torque is proportional to the effective magnetic moment, which depends upon the saturation magnetization, the domain state, and the dimensions of the nanowires. Thus, this dependence presents the opportunity to investigate the effects of the nanowire composition upon the alignment process.

Figure 6 shows the proportions of wires aligned within $0^\circ - 20^\circ$ of the applied field axis for Ni, Ni$_{0.8}$Fe$_{0.2}$, and Co nanowires. Since the nominal saturation magnetization of these wires are 485, 800, and 1440 emu/cm$^3$, respectively, it is simple to suggest increasing efficacy of field alignment from Ni through NiFe to Co nanowires. This trend is observed for the Ni and NiFe, but in contrast, the Co nanowires show the poorest field alignment. The effect of saturation magnetization upon the field alignment for NiFe nanowires may be complicated by the fact that these wires have a smaller diameter than the Ni and Co nanowires, although the relatively long length of the wires should minimise any differences in the demagnetizing factors. Nonetheless, comparing Ni and Co nanowires which have nominally identical geometries, the results show that the percentage of aligned Ni wires is higher than Co nanowires in all field strengths investigated (e.g., see Figure 4) and also that the proportion of Co nanowires aligned does not increase greatly above $\sim 200$ Oe (e.g., see Figure 5(a)).

To explain the compositional variation of the magnetic field alignment, both the magnetostatic shape anisotropy and the magnetocrystalline anisotropy need to be considered. In the case of Ni$_{0.8}$Fe$_{0.2}$, the intrinsic magnetocrystalline anisotropy is vanishingly small and the magnetization orientation will be controlled by the magnetostatic shape anisotropy to lie along the wire axis. The situation is likely to be similar for nickel as the intrinsic magnetocrystalline anisotropy is relatively low, so the magnetization will also be aligned along the wire axis. For nanowires with these two compositions, the alignment torque is then dependent upon the magnetic moment which will be larger for the NiFe than the Ni. In contrast to both NiFe and Ni nanowires where the crystal structure is face centred cubic (FCC), the crystal structure of Co nanowires is more complex and depends upon the deposition conditions and their diameter; so they may be FCC or hexagonal closed packed (HCP) (Refs. 3–5, 10, and 21) or some combination of the two phases. In both cases, the magnetocrystalline anisotropy is relatively large and may dominate the shape anisotropy. Indeed HCP, Co nanowires have
been shown to have a component of magnetization perpendicular to the wire axis.\textsuperscript{5,47,48} In this investigation, the crystalline structure of Co nanowires was studied by x-ray diffraction and found to be HCP.\textsuperscript{38} Therefore, it is suggested that the magnetic field alignment of Co is lower than for NiFe and Ni nanowires, because the dipole moment of the Co nanowires is not strongly developed along the wire axis; hence, the torque arising from the magnetic field is reduced. There is also the possibility of the differential formation of oxide or hydroxide layers on the surface of these nanowires during and after removal the alumina template that may adversely affect the magnetization of the Co nanowires. Thus, the magnetic field alignment is dependent upon the nanowire composition.

The fluid drag for a mid-point rotating nanowire has been approximated using a prolate spheroid approximation\textsuperscript{38} that indicates a very strong dependence upon the length of the structure and the viscosity of the suspension fluid. This dependence presents the opportunity to study the effects of the nanowires aspect ratio upon the alignment process. Therefore, a systematic study was performed to examine the effect of nanowire length on the alignment process in a magnetic field for Ni and NiFe nanowires. Figure 7 shows comparative histograms of the angular distribution for magnetic field deposited assemblages of NiFe nanowires with the wire lengths divided into two groups, one with wires less than 5 \( \mu \)m and the other with wires of length greater than 5 \( \mu \)m.

Clearly, there is a noticeable effect of nanowires length on the alignment process in all field strengths investigated here. The proportion of aligned wires for both lengths between 0°–10° for NiFe nanowires and within 0°–20° for Ni nanowires under application of different magnetic field strengths are summarised in Figures 8(a) and 8(b), respectively. The trend in these figures suggests a consistently higher percentage of aligned wires are obtained for longer nanowires at fields above \( \sim 200 \) Oe, where the percentage of long NiFe wires (\( \geq 5 \) \( \mu \)m) was found to be \( \sim 7\% \) within 0°–10° higher than shorter (<5 \( \mu \)m) wires, whereas this was \( \sim 12\% \) higher between 0° and 20° for long Ni wires than shorter wires (<5 \( \mu \)m). Thus, in all applications that require high percentage of aligned wires, it is very important to use wires with high aspect ratio.

![Fig. 7. An example of comparative histograms of percentage alignment for more and less than 5 \( \mu \)m length of 200 nm NiFe nanowires deposited at different field strengths (a) 100 Oe, (b) 500 Oe, and (c) 1 kOe.](image)
During the course of this study, a range of interesting features were observed resulting from magnetic field alignment. First, it was found that the nanowires can be oriented in any preferable direction by simply rotating the substrate with respect to the magnetic field during the deposition process without any noticeable effect on the orientation of the previously aligned and deposited wires. This behaviour is demonstrated in the scanning electron micrographs shown in Figures 9(a) and 9(b), which show Ni nanowires lying perpendicular to each other produced by deposition in two sequential steps using high magnetic field strength orientated normal to each other. This result agrees well with the other results in literature and demonstrates that the van der Waals and/or the electrostatic forces between the wires and the substrates are the dominant after deposition. This behaviour may be useful from a practical point of view in the fabrication of complex devices that need sequential steps of nanowire alignment, for example to create memory or logic architectures.

Another interesting observation is the formation of continuous chains of head-to-tail nanowires during deposition in applied magnetic fields, as demonstrated in Figures 9(c) and 9(d), which show scanning electron microscopy micrographs of parallel chains of Ni nanowires. The lengths of these chains were observed to extend over hundreds of micrometres, in agreement with the previous results. Depending upon the concentration, the location and distance between these wires in addition to the magnetisation, the viscous drag, and the magnetic field strength, the inter-wire dipolar interactions can play an important role in the formation of chains during the deposition process.

The final interesting feature is the formation of cumulative clusters of nanowires as demonstrated in scanning electron microscopy micrographs shown in Figures 9(e) and 9(f). The formation of these clusters could be attributed to the high concentration of nanowires during the deposition process, the low viscosity of the IPA, and large translational forces that result from strong applied magnetic fields. These clusters of nanowires are usually undesirable in fabrication of nano-devices or for further studies on the electrical and magnetic properties of isolated nanowires. Reducing the concentration of the wires in the IPA suspension was found to reduce this effect.

As outlined earlier, a variety of methodologies have been proposed and investigated for aligning of quasi-one dimensional nanostructures for technological applications. Here, the efficacy of magnetic field alignment has been...
quantitatively assessed using magnetic nanowires; however, the results may be relevant to a wider range of functional materials where these nanostructures are capped, coated, or incorporate magnetic material as demonstrated elsewhere. In solution, magnetic alignment imparts a high level of useful anisotropy to the material properties. These include, anisotropic polymer composites where electrical, electromagnetic, optical, or acoustic damping behaviour depends upon the anisotropy introduced by the aligned nanostructures. In solution, magnetic alignment of nanostructures can enhance thermal conductivity, and with fluorescent functionality, magnetic alignment has potential benefits for optical tracking in biotechnology applications. Magnetic alignment can also be effectively applied to control and manipulate mammalian cells.

For applications where site-specific location and orientation of nanostructures is required, such as electronic circuits and sensors, global magnetic alignment in conjunction with other methods for locating the nanowires onto specified positions on a device structure can assist in the orientation of nanowires. Such positioning techniques include chemical bonding via biochemical functionalization, localized electric field assisted alignment, and localized magnetic field gradients. For applications of nanowires in sensors, such as for biotechnology applications, where nanostructures need to make contact between electrodes, but the precise orientation of the nanowires is not significant, then magnetic alignment would be beneficial. For applications in other sensors, such as for magnetic field detection and for building electronic components and logic circuits that require high levels of precision in orientation and location, magnetic alignment of nanostructures alone does not provide a technical solution.

CONCLUSIONS

The effect of field strength, composition, and aspect ratio of electrodeposited Ni$_{0.8}$Fe$_{0.2}$, Ni and Co nanowires on the efficacy of magnetic field alignment of the nanowires was investigated. In the absence of magnetic field during the deposition process, the deposited nanowires were found to be randomly oriented on the substrates. However, under the application of different magnetic field strengths, the quality of the alignment was found to be strongly dependent upon the applied field. For all compositions investigated here, the percentage of oriented nanowires with the field axis was found to increase rapidly with increasing the magnetic field up to ~200 Oe and then increases slowly up to ~1 kOe for NiFe and Ni wires, whilst being constant for Co nanowires.

The highest percentage of aligned wires was obtained for the NiFe nanowires, whereas the lowest percentage of aligned wires was obtained for the Co nanowires, with the percentage alignment of Ni nanowires falling between the two. The compositional dependence of the alignment may be attributed to both saturation magnetization and the competition between magnetocrystalline anisotropy and shape anisotropy.

The effect of aspect ratio of nanowires on the alignment process was statistically investigated and was found to be ~7% higher for longer NiFe wires (≥5 μm) aligned within 0°–10° than for shorter wires (<5 μm) and was ~12% higher for longer Ni nanowires aligned between 0°–20° than for shorter wires (<5 μm).

ACKNOWLEDGMENTS

The authors would like to thank the British Council UK-India Education and Research Initiative (UKIERI) and the Indian DST for funding this collaborative research. Musaab S. Sultan also acknowledges help and financial support from the Iraqi government and the help from the staff of their Embassy in London.


