

Structural and magnetic properties of electrochemically grown Ni-Fe and Co-Fe nanowire arrays

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ABSTRACT

Nanowires of $\text{Ni}_{80}\text{Fe}_{20}$ and $\text{Co}_{90}\text{Fe}_{10}$ binary alloys were synthesized by direct current electrodeposition in polycarbonate templates. The purpose of this work is to understand the effect of pH and temperature of the bath on the structural and magnetic properties of these galvanostatically electrodeposited nanowires. The increase in both, pH and temperature of the bath, has resulted in the increase in the grain size of the textured $\text{Ni}_{80}\text{Fe}_{20}$ nanowires. The magnetic measurements have understandably demonstrated the shape anisotropy in nanowires. The observed variation in the coercivity with increase in deposition temperature can be correlated with change in the grain size.

Keywords: NiFe, nanowires, magnetic anisotropy, coercivity.

1 INTRODUCTION

Low dimensionality plays an important role in deciding the magnetic properties of materials and hence magnetic nanowires are an ideal playground for exploring the fundamentals of magnetism and spin related phenomena [1]. It has recently attracted considerable attention motivated by applications in the area of ultra-high-density perpendicular magnetic recording, read-heads and magnetic sensors [2]. The magnetic nanowire arrays filled in templates offer great potential for recording media because they can achieve a recording density of more than 100 Gbit/in² which is much higher than that of current commercial hard disks (3.7 Gbit/in²) [3]. Domain wall motion studies by magnetoresistance measurements on magnetic nanowires have emerged to be an exciting and interesting research area. Electrodeposition is a simple and important technique capable of depositing granular alloys [4], multilayers [5] and nanostructured materials, offering control over their structure, composition and properties [6]. Permalloy ($\text{Ni}_{80}\text{Fe}_{20}$) and CoFe alloys are excellent soft magnetic materials with very high initial permeability and low coercivity, mainly used in magnetic sensors, magnetic recording heads, motors, and generators for use in electric vehicles [7]. The deposition temperature controls the growth via the kinetics of depositing atoms in the porous

membranes so as to render the desired structure and magnetic properties. Lot of research efforts have been made to study the influence of deposition conditions on the properties of Co, Ni, Fe and their alloy nanowires [8]. Our aim is to study the effect of pH and temperature of bath on the structural and magnetic properties of alloy nanowires.

2 EXPERIMENTAL

Ni-Fe and Co-Fe nanowires are deposited in track-etched polycarbonate membranes of pore diameter 50 nm and pore length 6 μm . The deposition was carried in three electrode cell at different pH values (2.5 - 4.5) while varying bath temperature (30 -70°C) at each pH value from solution of 120 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 6 g/l $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 45 g/l H_3BO_3 for Ni-Fe alloy nanowires [9]. While the bath composition for Co-Fe nanowires is 120 g/l $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 13 g/l $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 45 g/l H_3BO_3 . The electrolyte pH was adjusted to the required value with either 10% H_2SO_4 or 25% NH_4OH . All solutions were prepared by dissolving reagent-grade chemicals in doubly deionised (DI) water. For depositing nanowires in PC templates, one side of the membrane is coated with Au layer of 150 nm thickness so that it can serve as working electrode. The electrochemical deposition was performed using computer controlled CHI-1100A workstation in the three electrode cell geometry. The cell consists of a standard calomel (Hg/ HgCl_2 / KCl) reference electrode and a 2 cm x 1.5 cm Pt sheet as the counter electrode. The deposition potential window (-1.0V to -1.2V) was estimated using cyclic voltammetry. The deposition was carried out at a constant current density of 2mA/cm² for duration of 100 to 200 sec in all the baths. The deposition temperatures were varied from 30 -70°C using the thermostat. The synthesized nanowires were subsequently characterized by Philips X'Pert X-ray diffractometer (40 mA, 45 kV) at a scanning rate of 3°/min. using Cu-K α radiation, ($\lambda=1.5406 \text{ \AA}$). The scanning electron microscope (SEM) images of the nanowires obtained on a ZEISS EVO-50 scanning electron microscope, operated at 20 kV. The transmission electron microscope (TEM) images and selected area diffraction pattern of the nanowires obtained on a CM 20 Philips TEM. The magnetic measurements were carried out on a vibrating sample magnetometer (VSM-EG&G Princeton Applied Research, Model-155).

RESULTS AND DISCUSSION

3.1 Structure and Morphology

The structural analyses of the nanowires deposited in PC membranes were done by X-ray diffraction in θ - 2θ mode. These X-ray diffractograms shows the presence of mainly Ni_3Fe phase with its (111) peak at $2\theta = 44.27^\circ$ (JCPDS - 38-0419). The nanowires are highly oriented in nature with (111) peak being prominent. The average grain sizes are calculated using Debye-Scherrer's equation:

$$D = \frac{0.9\lambda}{B_s \cos\theta}$$

where λ is the wavelength of the Cu-K α radiation, θ is the diffraction angle of (111) reflection and B_s is the FWHM of the diffraction line adjusted by pseudo-Voigt function.

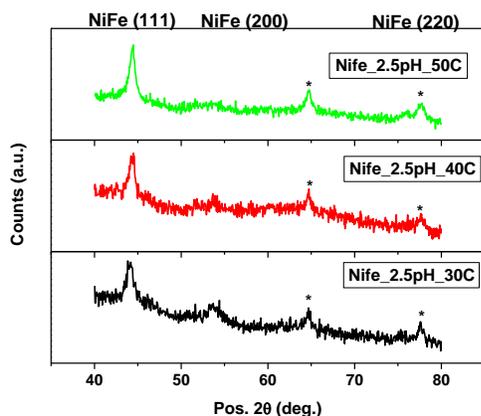


Fig 1. XRD patterns of NiFe alloy nanowires deposited at different temperatures from bath at pH=2.5

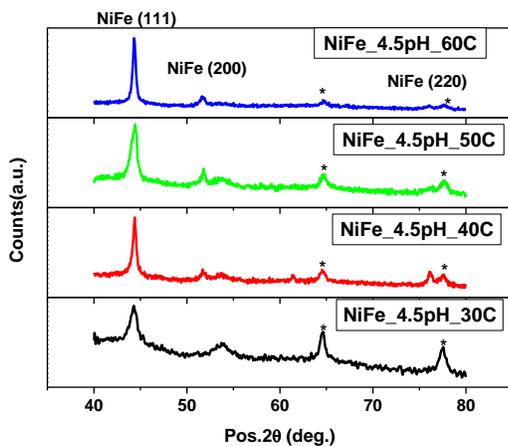


Fig 2. XRD patterns of NiFe alloy nanowires deposited at different temperatures from bath at pH=4.5

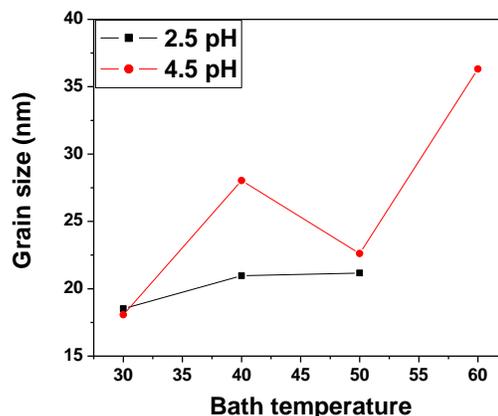


Fig 3. Variation of grain size with bath temperature

We observe an increase in grain sizes in different nanowires deposited at different bath pH and temperatures. The increase is from 18 nm at 30°C to 36 nm at 60°C in 4.5 pH bath while it increases from 18nm at 30°C to 21 nm at 50°C in 2.5 pH bath. Increase in grain size corresponds to the increase in rate of growth of nuclei with increase in deposition temperature. The TEM images show that the average diameter is about 100 nm. Selected area diffraction patterns show that NiFe nanowires are cubic single crystals while CoFe nanowires are highly textured crystallites having hexagonal structure.

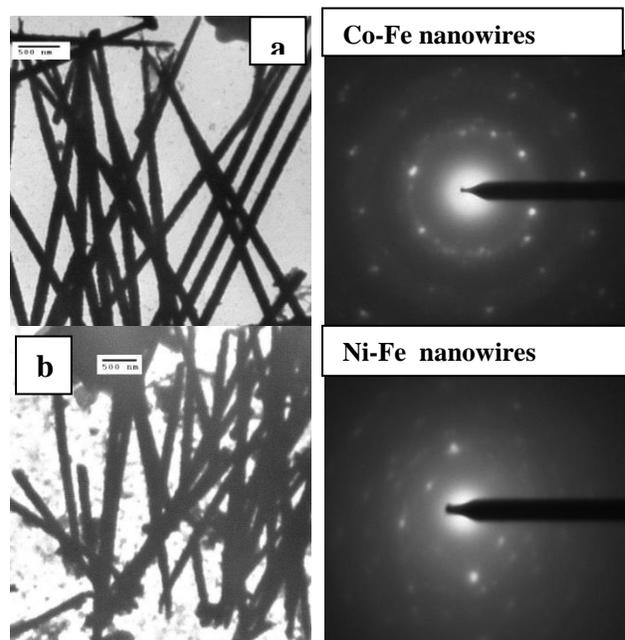


Fig 4. TEM images and SAED pattern of (a) Co-Fe nanowires and (b) Ni-Fe nanowires.

Energy dispersive X ray analysis shows that average composition of NiFe alloy nanowires deposited from above bath composition is 79 atomic % Ni and 21atomic % Fe while that of CoFe nanowires is 91 atomic % Co and 9atomic % Fe. Though the bath composition contains higher weight percent of Ni²⁺/Co²⁺ ions to Fe²⁺ ions. In case of iron alloy baths, it is well known that Ni and Co deposition is suppressed by the existence of Fe²⁺ ions and the less noble Fe preferentially deposits as explained by the anomalous codeposition mechanism reported by Dahms et al [10].

3.2 Magnetic properties

The magnetic measurements of the electrodeposited NiFe nanowires were done by vibrating sample magnetometer (VSM) at room temperature. The measurements were performed with the magnetic field applied parallel and perpendicular to the axes of nanowires. The hysteresis loops of four samples shown in Fig. 5 and 6.

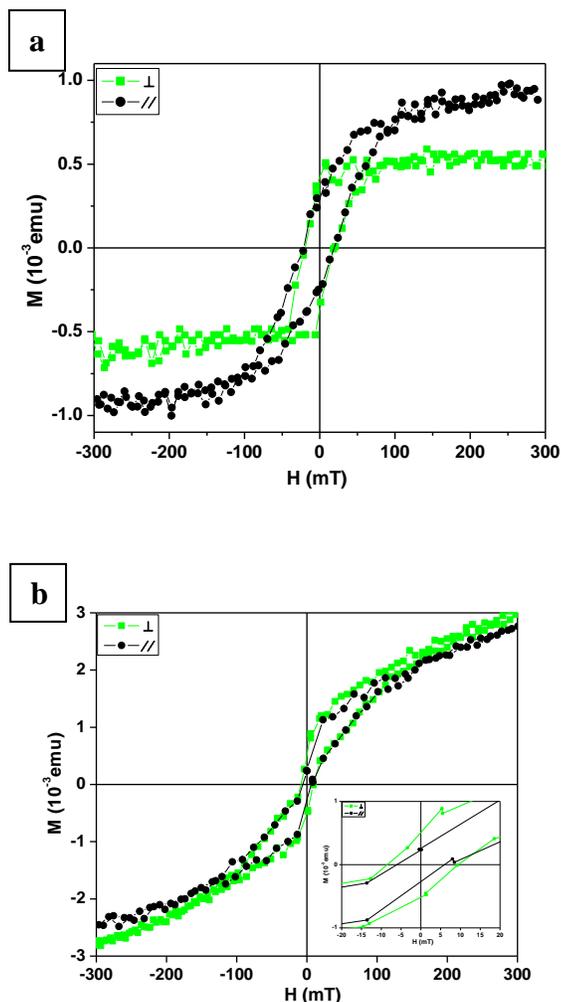


Fig 5. M-H curves NiFe nanowires deposited (a) at 4.5 pH and 30°C (b) at 4.5 pH and 60°C

Table 1

Sample Name	H _c ∥, along the NW axis (mT)	H _c ⊥, perp. to the NW axis (mT)
NiFe_2.5pH_30C	44.0	11.6
NiFe_2.5pH_40C	10.7	5.30
NiFe_2.5pH_50C	9.20	5.70
NiFe_2.5pH_60C	3.50	5.0
NiFe_4.5pH_30C	21.6	19.5
NiFe_4.5pH_40C	17.0	18.5
NiFe_4.5pH_50C	26.0	28.5
NiFe_4.5pH_60C	6.0	8.50

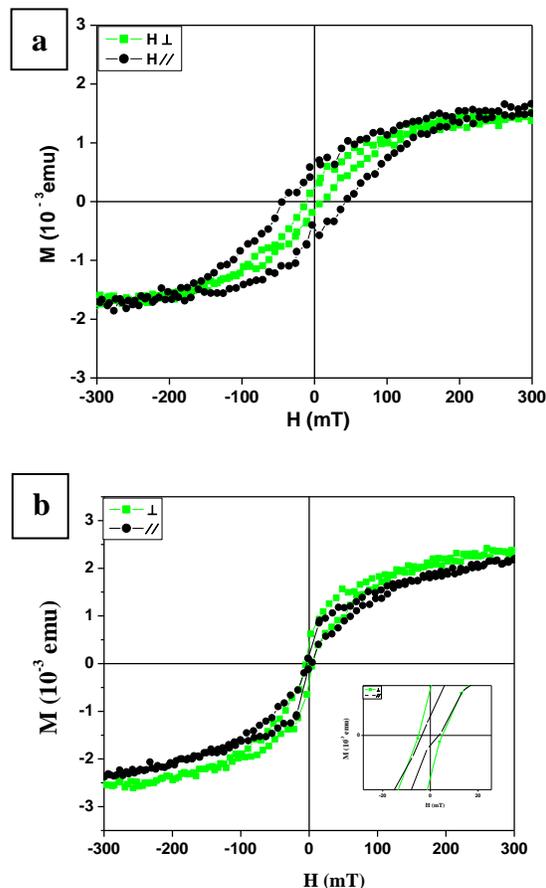


Fig 6. M-H curves NiFe nanowires deposited (a) at 2.5 pH and 30°C (b) at 2.5 pH and 60°C

The nanowires are easily magnetized along their axes. For a rod-shaped ferromagnetic entity, the demagnetizing factors for fields applied along and perpendicular to the rod axis are approximately 0 and 2π respectively. In the absence of an external field, the shape anisotropy compels the magnetization to be along the axial direction. The highly desirable perpendicular magnetization is a natural consequence of the geometry of the ferromagnetic nanowire array [11] and so the coercivity values differ along these

two directions. The observed coercivity is less than the theoretical calculated value due to shape anisotropy field, $H_k=2\pi M_s$. This could be due to imperfections which include compositional inhomogeneities along the wire, the shape of wire ends, wire diameter fluctuations as well as the intrinsic stress in the deposited nanowires [12]. As given in table 1, the coercivity values seems to show the inter dependence on the pH and bath temperature. At lower pH of 2.5, the coercivity values along the nanowires, $H_{c\parallel}$ are much larger than the coercivity values perpendicular to the nanowires, $H_{c\perp}$ at all temperatures. However, at this pH when the temperature is increased, the ($H_{c\parallel} - H_{c\perp}$) difference keeps on decreasing till at a higher temperature of 60°C, coercivity perpendicular to the nanowires, $H_{c\perp}$ becomes higher than coercivity along the nanowires, $H_{c\parallel}$. In contrast at a higher pH of 4.5, the ($H_{c\parallel} - H_{c\perp}$) difference is very small and the $H_{c\perp}$ becomes higher than $H_{c\parallel}$ at a low temperature of 40°C. The coercivity depends on various factors such as grain size, orientation of individual grains within a nanowire and dipolar interaction between the nanowires.

4 CONCLUSIONS

$Ni_{80}Fe_{20}$ alloy nanowires are successfully fabricated at different pH and temperatures. The coercivity measured parallel and perpendicular to nanowire axis shows interesting inter dependence on bath deposition temperature and bath pH values. Coercivity values with a low of 3.5 mT and a high of 44 mT were tunable by changing bath temperature from 30 to 60 C only. The XRD and TEM results jointly indicate that individually the nanowires are single-crystalline like in nature, but collectively they show a highly oriented growth.

REFERENCES

- [1] V. Rodrigues, J. Bettini, Paulo C. Silva, and D. Ugarte, Phys. Rev. Lett., 91, 096801, 2003.
- [2] A. Blondel, J. Meier, B. Doudin, and J.-Ph. Ansermet, Appl. Phys. Lett. 65, 3019, 1994.
- [3] R.M. White, R.M.H. New, and R.F.W. Pease, IEEE Trans. Magn. 33, 990, 1996.
- [4] G.R. Pattanaik, D.K. Pandya and Subhash C. Kashyap, J. Electrochem. Soc. 149, C363-369, 2002
- [5] D. K. Pandya, P. Gupta, Subhash C. Kashyap, and S. Chaudhary, J Mag Mag Mat 321, 974-978, 2009
- [6] I. Bakonyi and L. Peter, Prog. in Mat. Science, 55 107-245, 2010.
- [7] F. Pfeifer and C. Radloff, J. Mag. and Mag. Mat., 19 190-207, 1980
- [8] Y. Rheem, B. Yoo, B. K. Koo, and N. V. Myung, Phys. stat. sol. (a) 204, No. 12, 4021–4024 (2007)
- [9] T. Ohgai, L. Gravier, X. Hoffer and J.Ph. Ansermet J. Appl. Electrochem. 35, 479–485, 2005.
- [10] H. Dahms and I.M. Croll, J. Electrochem. Soc., 112 771, 1965.
- [11] S. Yang, H. Zhu, D. Yu, Z. Jin, S. Tang, Y. Du, J. Mag. and Mag. Mat. 222, 97-100, 2000.
- [12] C.-L. Xu, H. Li, G. Y. Zhao, H.L. Li, Applied Surface Science, 253, 1399–1403, 2006.