

INFLUENCE OF BATH COMPOSITION ON THE ELECTRODEPOSITED Co-Ni-P NANOWIRES

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Abstract. *CoNiP nanowire arrays were fabricated by electrodeposition method into polycarbonate (PC) templates at different pH values. It is obvious that the crystal structure of the CoNiP nanowires depends on the pH values of electrolyte. The XRD results show that crystal structure of the CoNiP nanowires is hcp structure and the intensity of the hcp (002) increased enhances as solution pH =5. Magnetic measurements indicate a dependence of the squareness and the coercivity of the magnetization hysteresis loop on pH values with a maximum coercivity of 1425 Oe. The morphological properties of CoNiP nanowires were studied by transmission electron microscopy (TEM). The chemical composition was determined by examination of the energy dispersive X-ray (EDS) spectra and the magnetic properties were measured by vibrating sample magnetometry (VSM).*

Keywords: electrodeposition, nanowire arrays, magnetic anisotropy, pH values, CoNiP.

I. INTRODUCTION

In recent years, magnetic nanowires have attracted much attention because of their unique magnetic properties and application potential for cell separation, biosensing, gene delivery, high density recording, high frequency sensors and others devices [1–5]. Tanase et al. studied the spatial organization of mammalian cells using ferromagnetic nanowires in conjunction with patterned micromagnet arrays [3]. The polycarbonate template has been widely used to prepare nanowire arrays because which plays an importance role in the synthesis of one dimensional nanomaterials. Today, among the various methods used to produce magnetic nanowire arrays into polycarbonate

template such as sputtering, sol-gel and chemical vapour deposition, ion beam but the electro deposition method is a simple technique, low cost, easily controlled methods and operates at room temperature. Many arrays of magnetic nanowire arrays such as Fe, Co, Ni and their alloys have been prepared based on this method [6–10]. In the present paper, we have produced of CoNiP nanowires by the electrodeposition into porous polycarbonate templates with influence of bath composition and various pH values.

II. EXPERIMENTAL

The magnetic nanowires of CoNiP were electrochemically deposited into the porous of a polycarbonate template. The polycarbonate template had a thickness about $3 \sim 5 \mu\text{m}$ with pore diameter about 200 nm. Before electrodeposition, a copper (Cu) layer of thickness about 200 nm was sputter - deposited onto one side of the polycarbonate template and used as the working electrode to fabricate magnetic nanowires.

The electrolyte used to electrodeposit the CoNiP nanowires had the following composition of 0.2M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; 0.2M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; 0.25M NaH_2PO_2 ; 0.7M H_3BO_3 ; 0.001M Sarcosine. The pH value of the electrolyte bath was adjusted from 3.0 to 7.0 by HCl or NaOH solution. Afterward, the polycarbonate template placed in the electrolytic bath. A three electrode bath was used for the electrochemical experiments. An Ag/AgCl electrode was used as the reference electrode (*RE*), the counter electrode was a platinum mesh (*CE*) and the working electrode (*WE*). The electrodeposition process was performed at a constant potential of 0.9 V in 20 minutes at room temperature. In this paper, the morphology of the CoNiP nanowires was investigated by mean of scanning electron microscopy (SEM). The crystal structure was analyzed by X-ray diffraction (XRD). Magnetization curves were measured using a vibrating sample magnetometer (VSM) in fields up to 10000 Oe. The nominal elemental composition of the nanowires was performed by energy dispersive spectroscopy (EDS).

III. RESULTS AND DISCUSSION

III.1. Morphological structure

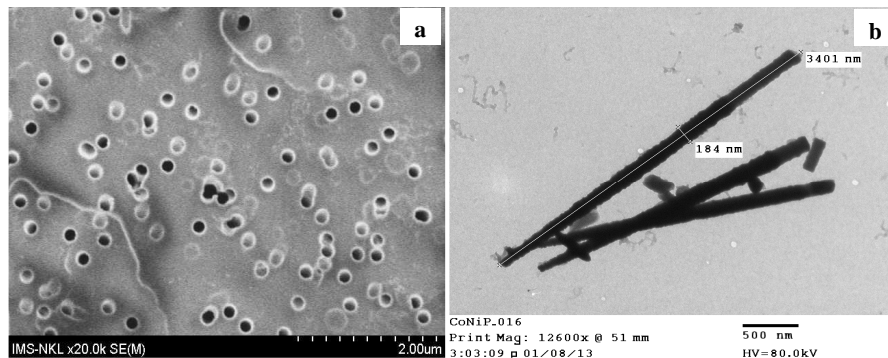


Fig. 1. (a) SEM image of the polycarbonate template with an average pore size of 200 nm and (b) TEM image of CoNiP nanowires with the diameter of 200 nm after removing the polycarbonate template.

Fig. 1 shows the SEM image of the polycarbonate template and TEM results of CoNiP nanowires with an average diameter of 200 nm. Fig. 1(a) demonstrates that the pore diameter of the polycarbonate template is about 200 nm and pores are almost uniform. CoNiP was electrodeposited into the pores of polycarbonate template. The magnetic nanowires of CoNiP were separated from the polycarbonate template by dissolving the template in chloroform as shown in Fig. 1(b). One can see that the magnetic CoNiP nanowires have the diameter about 200 nm and length above $3\mu\text{m}$ which are approximately equal to the pore diameter of polycarbonate template. The aspect ratio (L/d) of wires is greater than 18. From the TEM results, it can be estimated that the CoNiP nanowires was fabricated by electrodeposition method.

III.2. The microstructure

In order to study the structure of CoNiP nanowires, XRD was used to analyse the microstructure of the samples. Fig. 2 shows the XRD patterns of CoNiP nanowires deposited at different pH value. The differences of crystal structures are observed from the three patterns, the crystal structure of CoNiP nanowires is strongly dependent on the pH values of electrolyte.

All the CoNiP nanowires exhibited hcp structure and the intensity of the hcp (002) plane increased as solution pH value increased and reach their largest at pH = 5.0, and then decreases with further increase of pH = 7.0. The diffraction peaks appears at 41.83° shows the NiP phases which is attributed to the intermixing of the NaH_2PO_2 in the solution. The peaks appears at 44.9° corresponding to the CoNiP- hcp (002) phases and the intensity of the hcp (002) peaks enhances at pH = 5. This structure is consistent with the published results of of D.Y. Park. [11]. This result indicates that the appearance and enhancement of the diffractions of hcp (002) can be adjusted by increasing of the pH value of the electrolyte. The copper (Cu) peaks are due to the copper film sputtered on the surface of the polycarbonate template.

III.3. Chemical composition

The elemental composition of the CoNiP was measured by energy dispersive analysis by X-rays. Fig. 3 shows the EDX spectrum analysis. The nanowires consist only Co, Ni and P. Cu peaks are due to the copper film sputtered on the

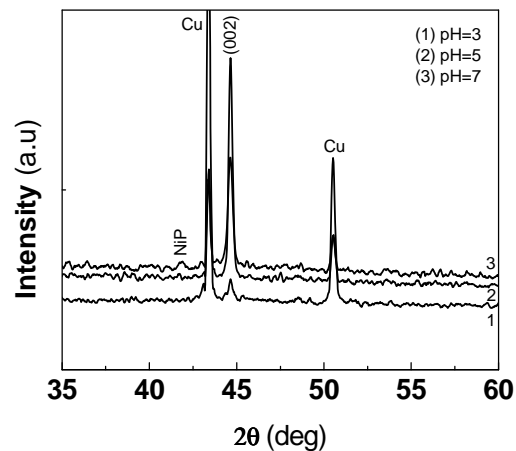


Fig. 2. XRD patterns of CoNiP nanowires at various solution pH values

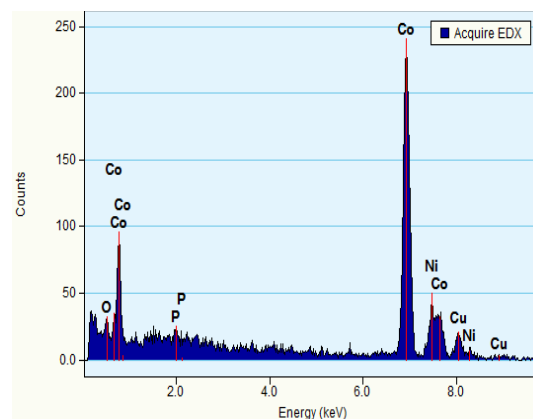


Fig. 3. EDX spectrum analysis of CoNiP nanowires

surface of the sample. From this figure it can be confirmed that there is no other elemental impurities are present in the nanowires composition. The copper and oxygen peaks are due to the copper film sputtered on the surface of the polycarbonate template. According to the results of the (EDX), the CoNiP nanowires were obtained with variable composition as a function of the solution composition. Low P % atomic was observed in all the cases (Table 1). The deposit Co content decreased from 81.20 at% to 63.42 at% and the deposit Ni content increased from 12.00 at% to 27.88 at% corresponding to increasing pH values from 3.0 to 7.0.

Table 1. Composition of the CoNiP nanowires with different pH values

pH	Co (at%)	Ni (at%)	P (at%)
3.0	81.20	12.00	6.80
5.0	68.54	18.36	13.10
7.0	63.42	27.88	8.70

IV. MAGNETIC PROPERTIES

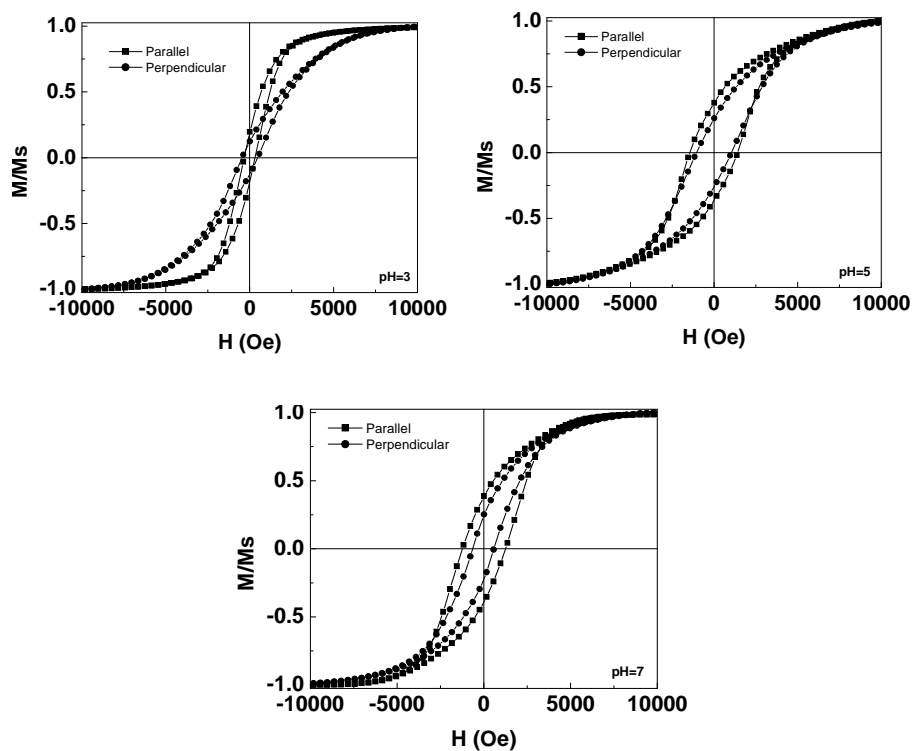


Fig. 4. Hysteresis loops for an 200 nm diameter CoNiP nanowires in PC template

Fig. 4 shows the magnetization hysteresis loops of CoNiP nanowire arrays with the different pH value. It demonstrates that the easy axis of magnetization direction is parallel to the long axis of the nanowire.

It can be seen that in both cases of parallel and perpendicular to the wire, the squareness (M_r/M_s) and the coercivity (H_c) of the magnetization hysteresis loops increase with increasing pH values, and achieve their maximal values at pH = 5.0, and then decrease with increasing of pH = 7.0.

Namely, with a field parallel to the wire axis, the squareness of CoNiP nanowires increase from 0.19 to 0.38 and with a field perpendicular to the wire axis the squareness of CoNiP nanowires increase from 0.12 to 0.26 corresponding to increasing of the pH values from 3.0 to 5.0. The coercivity of the CoNiP nanowires with magnetic field placed parallel to the wire increase from 320 Oe to 1425 Oe and when the applied field was perpendicular to the nanowire, the coercivity of the nanowires increase from 480 Oe to 1070 Oe as the pH values increase from 3.0 to 5.0. However, when increased to pH = 7.0, the coercivities with the applied field parallel and perpendicular to the nanowire are 1250 Oe and 570 Oe, respectively.

In addition, for values of pH = 5.0, it can be observed that the two loops measured in parallel and perpendicular fields are almost overlapping. In other words, it is an obvious decreasing of magnetic anisotropy along wire axis.

V. CONCLUSIONS

We have prepared CoNiP nanowires with diameter of 200 nm and length above 3 μm by the electrodeposition method. The crystallographic structure of the CoNiP nanowires and the magnetic properties of the nanowires are dependent on the pH of electrolyte. At the solution of pH = 5.0, the intensity of the hcp (002) peak of the CoNiP nanowire is strongly enhanced and a maximum coercivity of 1425 Oe is obtained with magnetic field applied parallel to the wire.

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