

Influences of pH Values on Magnetic CoNiP Nanowires Fabrication

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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=3.5. Magnetic measurements indicate that CoNiP nanowires show a transition from soft to hard magnetic properties with pH values from 2.0 to 3.5 and the maximum coercivity is 1630 Oe.

Keywords: PC template, CoNiP nanowires, magnetic properties and electrodeposition.

1. Introduction

Magnetic nanowires have received much attention in the last few years because of their unique magnetic properties and application potential for cell separation, biosensing and gene delivery [1- 4]. Hultgren et al studied the application of Ni nanowires in cell separation [5]. It was found that high purity separations can be achieved for nanowires over a wide range of size, while the optimum separation yield is achieved when the average length of the nanowires matches the average diameter of the cell. In fact, the magnetic properties of magnetic nanowires are related to many parameters of the nanowire, such as length, diameter and composition. To date, many different techniques have been employed to produce nanoscaled materials. Among them, the electrodeposition of nanowires into polycarbonate template is a simple, low cost and operates at room temperature. Template synthesis based on ordered polycarbonate membrane has attracted much interest because of their wide application in fabricating nanowire and nanotube arrays [6]. Therefore, Ni, Fe, Co and their alloys nanowires have been produced into polycarbonate membrane with template synthesis methods.

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In the present paper, we have produced of CoNiP nanowires by the electrodeposition into porous polycarbonate templates with various pH values.

2. Experimental

At first, we have used porous polycarbonate template with pore diameter of 200 nm and thickness about 5 μm . 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. 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 electrolyte used to electrodeposits 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 Sarcchrin. The pH value of the electrolyte bath was adjusted from 2.0 to 3.5 by HCl or NaOH solution. The electrodeposition process was performed 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).

3. Results and discussion

Fig.1 shows the SEM image of the polycarbonate template and SEM 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. Fig. 1(b) shows that the magnetic CoNiP nanowires have the diameter of 200 nm and length about 5 μm which are approximately equal to the pore diameter of polycarbonate template. From the SEM results, it can be estimated that the CoNiP nanowires was fabricated by electrodeposition method.

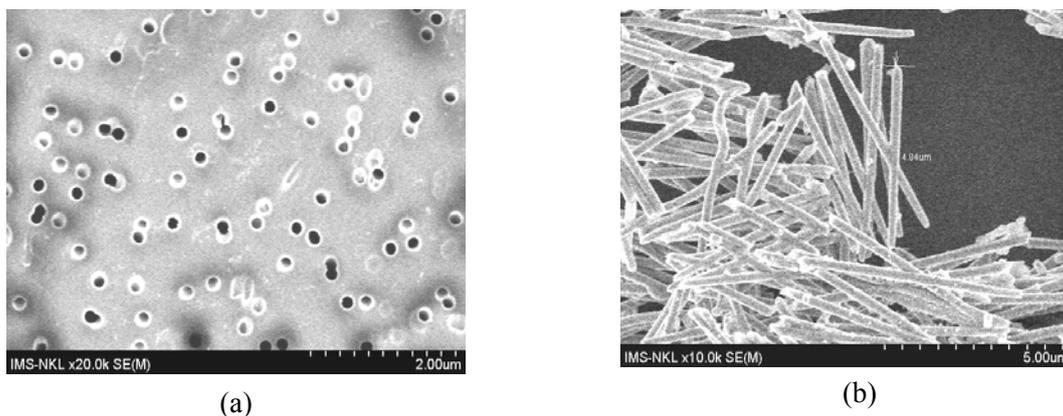


Fig.1. (a) SEM image of the polycarbonate template with an average pore size of 200 nm and (b) SEM image of CoNiP nanowires with the diameter of 200 nm after removing the polycarbonate template.

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. The diffraction peaks appears at 39° shows the mixture of NiP or CoP phases which is attributed to the intermixing of the NaH_2PO_2 in the solution.

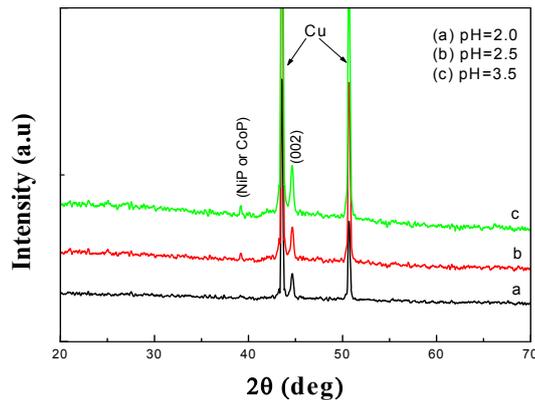


Fig.2. XRD patterns of CoNiP nanowires at various solution pH values.

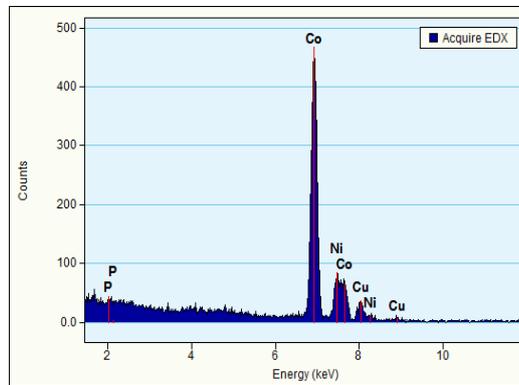


Fig. 3. EDX spectrum analysis of CoNiP nanowires.

The peaks appears at 44.9° corresponding to the CoNiP - hcp (002) phases and the intensity of the hcp (002) peaks enhances at pH=3.5. This structure is consistent with the published results of D.Y. Park. [7]. 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 corresponding to the P content increases. The copper (Cu) peaks are due to the copper film sputtered on the surface of the polycarbonate template.

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 surface of the sample.

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

pH	Co (at%)	Ni (at%)	P (at%)
2.0	84.20	9.80	6.00
2.5	83.55	10.15	6.30
3.5	75.74	17.10	7.16

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 84.20 at% to 75.74 at% and the deposit P content increased from 6 at% to 7.16 at% corresponding to increasing pH values from 2.0 to 3.5.

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. In both cases of parallel and perpendicular to the wire, the coercivity (H_c) and squareness (M_r/M_s) increases with increasing of the pH values.

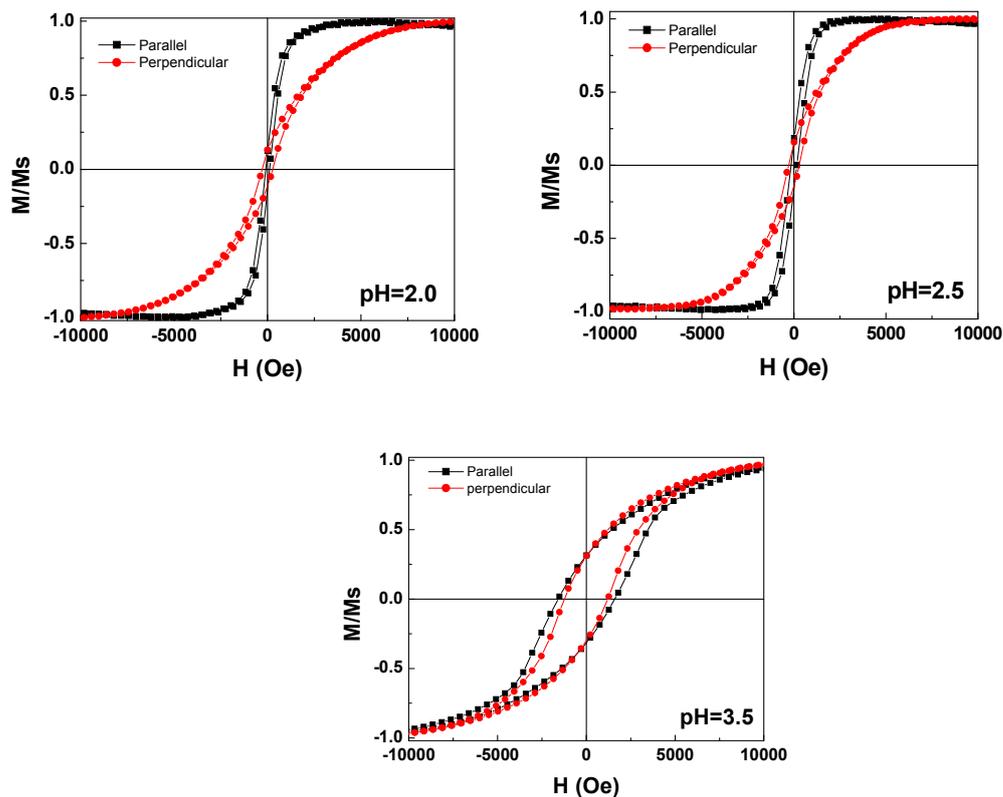


Fig.4. Hysteresis loops for an 200 nm diameter CoNiP nanowires in PC template

These changes in the coercivity are related to the appearance and enhancement of the P concentration. The squareness of CoNiP nanowires increase from 0.11 to 0.32 with increasing of the pH values from 2.0 to 3.5. The coercivity of the CoNiP nanowires with magnetic field placed parallel to the wire increase from 105 Oe to 1630 Oe and when the applied field was perpendicular to the nanowire, the coercivity of the nanowires increase from 263 Oe to 1270 Oe as the pH values increased. In addition, the CoNiP nanowire arrays show a transition from soft to hard magnetic properties as the pH values increased from 2.0 to 3.5 corresponding to increasing P concentration in the solution. The maximum coercivity is about 1630 Oe and the maximum squareness is 0.32 at pH=3.5.

4. Conclusions

In summary, we have prepared CoNiP nanowires with diameter of 200 nm and length of 5 μm by the electrodeposition method. The crystal structure of the CoNiP nanowires is dependent on the pH of electrolyte and the intensity of the hcp (002) increased enhances as solution pH=3.5. The magnetic properties of the nanowires depend on the pH values in the solution and the maximum coercivity value is 1630 Oe. Increasing the P contents from 6.00 at% to 7.16 at% resulted in a transition from soft to hard magnetic properties corresponding to pH values from 2.0 to 3.5.

Acknowledgments

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