Magnetic Behaviors of Arrays of Co-Ni-P Nanorod: Effects of Applied Magnetic Field

Luu Van Thiem¹, Pham Duc Thang¹, Dang Duc Dung², Le Tuan Tu^{3,*} and CheolGi Kim⁴

¹Faculty of Engineering Physics and Nanotechnology, VNU University of Engineering Technology, Vietnam National University, 144 Xuan Thuy, Cau Giay, Ha Noi, Viet Nam

²Department of General Physics, School of Engineering Physics, Ha Noi University of Science and Technology, 1 Dai Co Viet road, Ha Noi, Viet Nam

³Faculty of physics, VNU University of Science, Vietnam National University, 334 Nguyen Trai, Thanh Xuan, Ha Noi, Viet Nam

⁴Department of Materials Science and Engineering, Chungnam National University, Daejeon 305-764, South Korea

The Co-Ni-P nanorods were fabricated by electrodeposition method by using the porous polycarbonate template. The investigation by mean of X-ray diffraction and high-resolution transmission electron microscopy indicated that samples were nanocrystalline clusters embedded in the amorphous base. The samples exhibited a room temperature ferromagnetism with the high magnetic anisotropy along the rod. The applied magnetic fields during the fabrication of the Co-Ni-P nanorods was strongly influenced by the magnetic properties. The M_R/M_S ratio and coercivity rapidly increased when the magnetic applied field changed from 0 to 0.21 T. [doi:10.2320/matertrans.MA201520]

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1. Introduction

Recently, low-dimensional magnetic materials has attracted much attention of scientists in both theoretical and application aspects because of its high potential applications in ultra-high-density magnetic recording, magnetic resonance imaging, microwave absorber, microelectromechanical system, biomedical microdevices, and catalysis etc.¹⁾ The polycarbonate template has been widely used to prepare the nanowire arrays because of its importance role in the synthesis of one dimensional nanomaterials: control average diameter, periodicity, ideal cylindrical shape and the length of the nanowire arrays. Among the methods to produce the magnetic nanowires such as sputtering, sol-gel and chemical vapour deposition, the electrodeposition method is a simple technique, low cost, easily controlled methods and operates at the room temperature.²⁻⁴⁾

The Co-Ni based materials with nanorods and nanowires structure exhibited the enhance activities due to high shape anisotropy, chemical composition, size, and morphology.⁵⁻⁷⁾ In addition, the Co-Ni-P ternary alloy based nanowires exhibited hard magnetic properties with much higher coercivities than that of the individual Co and Ni nanowires.⁸⁾ Recently, X. He *et al.* reported that the addition of P content in Co-Ni nanowires resulted in the dramatic increase in the coercivities.⁹⁾ The hard magnetic properties with higher coercive fields (~ 0.2 T) were showed in CoPtP thin films due to the addition of hydrophosphite to the electrolyte.¹⁰⁾ Recently, a review work by Coey and Hinds for current fabrication of nanowires structure by using the magnetic electrochemistry indicated that the magnetic field could be used during the electrodeposition to enhance the deposition rate and also to induce the turbulent flow.¹¹⁾ Bund *et al.* reported that there was a clear dependence of the structural of the electrodeposited nickel via the external applied magnetic field during the deposition.¹²⁾

In this paper, we investigated the effects of varying the external applied magnetic field ($H_A = 0-0.21$ T) on the magnetic properties of Co-Ni-P nanorods with the diameter of 200 nm and the length of 3 μ m, which were electrodeposited into polycarbonate templates. We found that the magnetic properties of Co-Ni-P nanorods were improved when the external magnetic field was applied during the deposition. The value of squareness (M_R/M_S) and H_C rapidly increased when the applied magnetic field changed from 0 to 0.21 T. The magnetic anisotropy of Co-Ni-P nanorods are also studied.

2. Experimental Procedure

The Co-Ni-P nanorod samples were synthesized by using the polycarbonate templates with pore diameters of 200 nm and thickness of 3 μ m. The copper electrode was deposited to one side of the polycarbonate template via DC sputtering. A three electrode bath was used for the electrochemical experiments where Ag/AgCl electrode was used as the reference (RE), the counter electrode was a platinum mesh (CE) and the working electrode (WE). The solution of raw materials was $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, NaH_2PO_2 , H_3BO_3 and Sarcchrin which concentration was 0.2 M, 0.2 M, 0.25 M, 0.7 M and 0.001 M, respectively. The electrochemical potential of the solution was determined by cycle voltammetry. The applied potential during the fabrication of Co-Ni-P nanorod was -0.9 V and the pH values were controlled to 5.5 at room temperature. The strength of applied magnetic field (H_A) was 0; 0.075; 0.12; 0.15; and 0.21 T which were perpendicular to the polycarbonate template film, this means the magnetic field was applied in the parallel direction to the rod (along the rod long axis). The crystalline structure and morphology of the samples were characterized by X-ray diffraction (XRD, Advance D8, Bruker, Karlsruhe, Germany) and high-resolution transmission electron microscopy (HR-TEM, Tecnai G² 20 S-TWIN, FEI, Oregon, USA), respectively. The compositions of Co-Ni-P nanorod were confirmed

*Corresponding author, E-mail: letuantu@hus.edu.vn

by using the energy dispersive X-ray spectroscopy (EDX, Tecnai G² 20 S-TWIN, FEI, Oregon, USA). The hysteresis loops were measured at room temperature using the vibrating sample magnetometry (VSM, 7404, Lake Shore, OH, USA) with magnetic field applied perpendicular and parallel to the rod axis.

3. Results and Discussions

Figure 1 shows the X-ray diffraction patterns of the Co-Ni-P nanorods prepared without an external magnetic field (0 T) and with the magnetic fields of 0.075; 0.12; and 0.21 T during the deposition. The intensities of the Co-Ni-P nanorods peaks increased as increasing H_A in comparison with the intensities of Cu peaks as electrode. The main Co-Ni-P diffraction peaks were indexed as h -Co(002) phase with hexagonal structure. In addition, the small diffraction peak of α -Co(002) phase overlapped with the Cu(002) electrode were obtained. This result is consistent with that was previously reported by Rani *et al.*⁸⁾ The copper (Cu) peaks appeared to occur due to the copper film sputtered on the surface of the polycarbonate template.

Figure 2(a) shows the TEM of as-deposited Co-Ni-P nanorods. The length of Co-Ni-P nanorods was approximately 3 μm which were close to the size of porous polycarbonate using as template. The TEM images clearly

Fig. 1 The XRD patterns of as-deposited Co-Ni-P nanorod fabricated at difference strength of applied magnetic field during deposited with $H_A = 0; 0.075; 0.12; 0.15$; and 0.21 T.

indicated that clusters with crystalline structure were embedded in the amorphous Co-Ni-P base. Figure 2(b) shows the EDX spectra of Co-Ni-P nanorod as mark points in Fig. 2(a). All elements Co, Ni and P were identified in the spectra, indicating that the samples contain all of expected elements. The average concentration of Co:Ni:P was approximately 81 : 14 : 5. Moreover, the high resolution TEM of Co-Ni-P samples shows the spot dark separated along to nanorod, as shown inset of Fig. 2(a), indicating that the samples were inhomogeneous. The microstructure of Co-Ni-P nanorods was investigated by HR-TEM. Figure 3 shows the HR-TEM image of the two typical structures of Co-Ni-P nanorods prepared without an external magnetic field and with an external magnetic field of 0.21 T. As shown in Fig. 3(a), when no external field was applied, a layer atom structure of the nanorods was observed, but the structure was not clear. In Fig. 3(b), when the intensity of the applied external magnetic field increased to 0.21 T, the orientation of the Co-Ni-P nanoparticles is more quickly promoted and the result showed a layer-atom-like structure. The HR-TEM images indicated that the lattice space was determined to be about 0.205 nm.

Figure 4(a)–(f) shows the magnetic hysteresis loops (M - H) of Co-Ni-P nanorods deposited at the selected H_A values of 0; 0.075; 0.12; 0.15; and 0.21 T during the deposition, respectively. The magnetic signals were recorded in both parallel and perpendicular magnetic applied field direction to the nanorod axis at room temperature. The clear hysteresis loops obtained indicated that the Co-Ni-P nanorods exhibited hard magnetic properties at room temperature. In addition, the different shapes of M - H curve provided that the Co-Ni-P nanorods exhibited the high anisotropy when magnetic field was applied parallel and perpendicular to the rod axis. Our results are consisted with recently reported results for the magnetic anisotropy of Co-based nanorods which resulted from the shape anisotropy dominated over the magneto-crystalline.¹³⁾ Moreover, the M - H loops became square as H_A increased which is a strong evidence for influence of applied magnetic field during deposited on the magnetic properties of Co-Ni-P nanorods. The effects of H_A to the magnetic properties of Co-Ni-P nanorod were shown in Fig. 5. Figure 5(a) shows the deduction of M_R/M_S ratio as function

Fig. 2 (a) TEM images of as-deposited Co-Ni-P nanorod, and (b) the EDX spectral of as-deposited Co-Ni-P nanorod. Inset of Fig. 2(a) show the high magnification of TEM image.

Fig. 3 HR-TEM images of as-deposited Co-Ni-P nanorod fabricated at difference strength of applied magnetic field during deposited: (a) $H_A = 0$ T and (b) $H_A = 0.21$ T.

Fig. 4 The M-H curves of as-deposited Co-Ni-P nanorods at room temperature in both applied magnetic fields in parallel and perpendicular direction to the rod for H_A values of (a) 0 T; (b) 0.075 T; (c) 0.12 T; (d) 0.15 T; and (e) 0.21 T.

of H_A applied in both directions where M_R and M_S values are the remnant and saturation magnetization, respectively. The Co-Ni-P nanorods without applying field H_A exhibited the M_R/M_S values 0.51 and 0.25 in parallel and perpendicular direction, respectively. These values increased to 0.74 and 0.33, respectively, when magnetic field was applied during the deposition. To further understanding the mechanism of influence of M_R/M_S ratio of the $M-H$ loops via applied magnetic field during deposited, the possible diagram of rotation magnetic moment of magnetic clusters was presented. Figures 5(c)–(e) show diagrams of possible magnetic moment of crystalline clusters embedded in Co-Ni-P nanorod, where magnetic moments rotate with applied magnetic field to along the rod. In addition, the crystallites were randomly embedded on the surface of the amorphous nanorods, so the magnetic anisotropy of the nanorods is given by the shape anisotropy and magnetocrystalline

anisotropy, but the main origin of the magnetic anisotropy is shape anisotropy. The effect of H_A to coercivity of Co-Ni-P nanorods shown in Fig. 5(b). The coercivity increased from 0.19 to 0.23 T when magnetic field deposition increased from 0 to 0.21 T in the parallel to the nanorod. The coercivity values increased in both parallel and perpendicular to the rod when samples deposited under applied magnetic field. However, the coercivity values in the parallel to the rod were larger than that of the perpendicular to the rod.

4. Conclusion

The Co-Ni-P nanorods were fabricated by using electro-deposition method with polycarbonate supported as template. The nanocrystalline embedded along the amorphous nanorods. All the Co-Ni-P nanorods exhibited h-Co(002) phase with hexagonal structure and the intensity of h-Co(002)

Fig. 5 The dependent of strength magnetic applied field to (a) the deduction of M_R/M_S ratios and (b) the coercivity in parallel and perpendicular to the Co-Ni-P nanorods. (c)–(e) The proposal diagram of rotation magnetic moment of clusters along the nanorods under strength of applied magnetic field during deposited.

increased more significantly when the magnetic applied field changed from 0 to 0.21 T. The magnetic properties of Co-Ni-P nanorods were improved when the external magnetic field was applied during the deposition. The value of squareness (M_R/M_S) and H_C rapidly increased when the magnetic applied field changed from 0 to 0.21 T. The magnetic anisotropy of Co-Ni-P nanorods is the shape anisotropy.

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