

Synthesis and Magnetic Properties of NiCo Nanowire Array by Potentiostatic Electrodeposition

Ying Cao, Guoying Wei^{1,*}, Hongliang Ge^{2,*}, Yundan Yu

College of Materials Science and Engineering, China Jiliang University, Hang Zhou 310018, China

*E-mail: guoyingwei@sina.com; gehongliang@sina.com

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NiCo alloy nanowires have been fabricated by electrodeposition using anodized aluminum oxide templates. Growth of nanowires consists of four different stages namely nucleation, steady state growth, filling of pores, and coverage of filled nanowires on the temple surface. SEM study of nanowires showed that the as-obtained nanowires exhibit a uniform diameter of about 100nm. It is found that the crystal texture of the NiCo nanowires depends on the external potential value during electrodeposition. A highly preferential orientation () of the NiCo nanowires has been observed by XRD measurements. The magnetic properties of NiCo nanowire arrays determined by VSM are associated with the deposited potential. The maximum value of saturation magnetization to the array is 924 emu/cm², while the value of coercivities is 145 Oe. Saturation magnetization increases with the deposition potential. This work also demonstrates that nanostructure and properties of nanowires can be achieved through careful control of the deposition potential.

Keywords: NiCo nanowire, Electrodeposition, SEM, Magnetic property;

1. INTRODUCTION

Magnetic nanomaterials have attracted extensive interest in recent years because of their fundamental properties and wide range of applications, particularly for magnetic memories or MEMS [1-4], catalysis, and medical fields [5-6] such as high-density data storage [7] and magnetic field sensors [8].

Various methods are used to prepare magnetic nanowires with controlled length, diameter and properties. Morphological control and synthesis of complex nanowire structures present a challenge. Because of the unique density of electronic states nanowires in the limit of small diameters were expected to exhibit significantly different optical [9], electrical [10] and magnetic properties [11] from

their ordered three-dimensional nanostructures. The attractive properties of one dimensional system arise from their unique chemistry [12] and physics properties [13].

In this work, NiCo nanowires were deposited through the double alumina template method. Moreover, by controlling the deposition parameter, we have also investigated the electrochemical growth behavior of the NiCo alloy nanowires with emphasis on the SEM and TEM observations and electrochemical current transient curves.

2. MATERIALS AND METHODS

NiCo magnetic nanowires were grown by electrodeposition using a commercial alumina template (Two-step anodizing method) which has an array of holes with the size of $1.25 \mu\text{m}^2$ area and 80-100 nm in diameter. A thin conducting layer of pure copper (Cu) was sputtered on one side of each template served as a working electrode for electrodeposition. An electrical contact was made insulating tape so that only holes on the other side of the template were exposed. The template was then submerged in an electrolytic solution containing 0.2 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.1 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.4 M H_3BO_3 and 3 mg/L $\text{C}_6\text{H}_8\text{O}_3$. The electrodeposition cell consists of vertically positioned electrodes: a working electrode prepared in the method described above, graphite was used as a counterelectrode, and the saturation KCl reference electrode. The current transient curves were obtained at 30°C . The nanowires were electrodeposited through direct current deposition. The alumina templates of the samples were etched partially using a 4 mol/L NaOH solution in order to expose the nanowires to the X-ray beam. The morphology of NiCo nanowires was observed by transmission electron microscopy (TEM). X-ray diffraction (XRD) was used to investigate the microstructure of the NiCo nanowires. The magnetic properties of NiCo nanowires were measured by vibrating sample magnetometry at room temperature with the maximum applied field of 20kOe.

3. RESULT AND DISCUSSION

Fig. 1 illustrates the schematic pictures of growing nanowires in AAO template. Structural differences between Al_2O_3 and NiCo alloy cause rapid growth of nanowires in central section with hemispherical head. Furthermore, as shown in Fig. 1, one side of AAO template were sputtered with layer of copper during the transfer from stage "a" to stage "b". Nanowires were grown on the copper substrate from stage "b" to stage "c". Then AAO templates were removed using 4 mol/L NaOH solution. Fig.2 shows the current transient curves for the growth of NiCo alloy nanowires. According to current transients for the NiCo deposition in Fig.2, there are different growth stages[14]: (1) after a current peak at the initial time due to the double layer formation on the template surface, the faradic current starts the nucleation of the nanowires. Progress in nucleation accelerates the current drop due to increase in mass transport limitations. (2) Steady state growth of nanowires starts with hemispherical head due to easier growth in central section of nanowires. (3) Metal ions start diffusion from "a" to "b". (4) NiCo nanowires begin to grow stably. Consequently, the electrodeposition current

will decrease due to the decrease in electroactive surface area. Under this situation, the total electroactive surface area is equal to the total exposed surface area of template in solution.

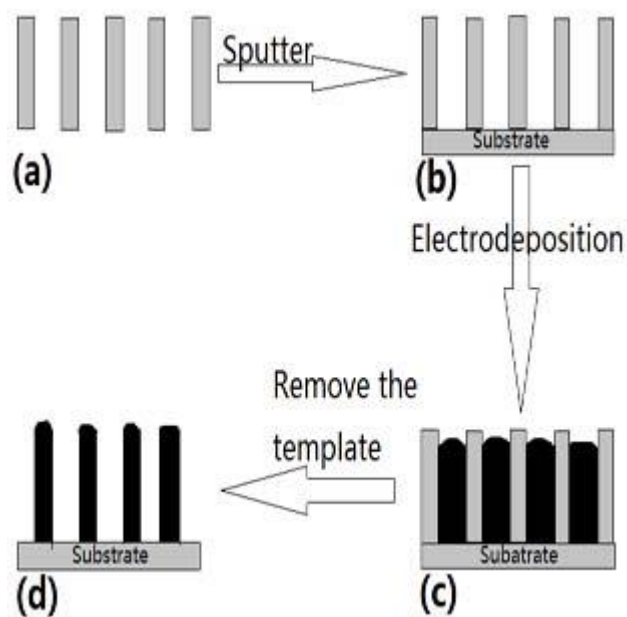


Figure 1. Schematic illustration of growing nanowires in AAO

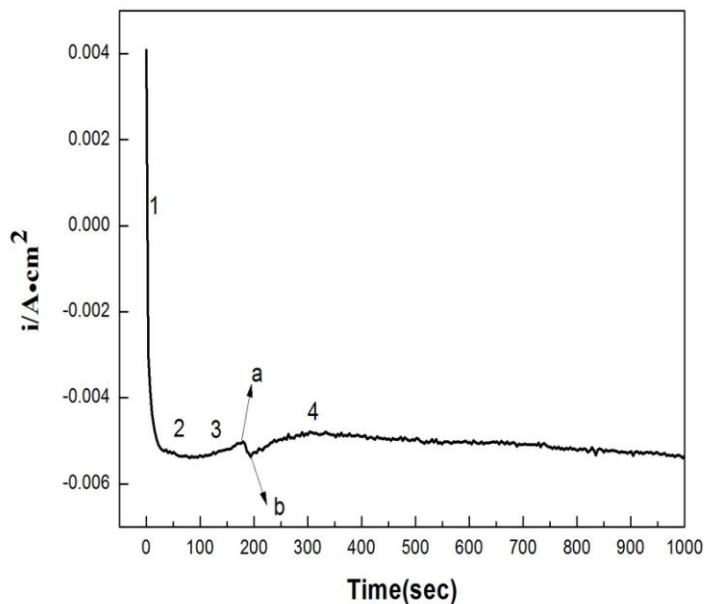


Figure 2. I-t transients for deposition of NiCo alloy nanowire (-0.8V)

Fig. 3(a) shows the SEM image of an alumina template prepared by a two-step anodic oxidation. From the image, the pores in the alumina template array in a regular style. It should be natural consequence for us to obtain highly ordered array by means of such a regular template. The

NiCo nanowires array prepared by template electrodeposition have been shown in Fig. 3(b) ~ (d). From Fig. 3(d), it can be seen that the diameter of the as-obtained nanowires is about 90nm corresponding to the size of pores in the alumina template. To observe the nanowires electrodeposited in the pores by SEM, the arrays have been dipped in 4 mol/L NaOH solution for 15 min to dissolve the upper alumina template so as to reveal the alumina template. The nanowires shown in Fig. 3(b) ~ (c) tend to be gathered into bunched structure. At the same time, the nanowires do not display an identical length. Therefore, it can be concluded that the deposition of NiCo nanowires is non-homogenous throughout the alumina template. Figure 3(d) is a transmission electron microscope diagram. The diameter of nanowire is relatively uniform and no step type seen in the figure. From these pictures, we know that the diameter of nanowires are constant in particular the diameter of the template.

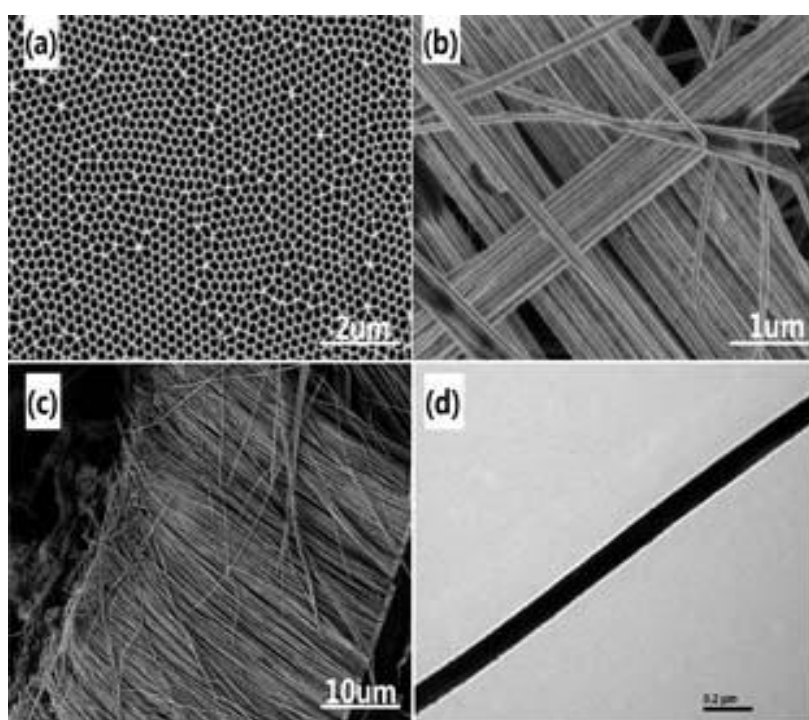


Figure 3. (a) SEM image of a porous alumina template; (b)~(c) Typical SEM micrograph of NiCo nanowires array by dissolving partly the alumina template in a 4 mol/L NaOH solution for 15min; (d) TEM images of NiCo alloy nanowires.

The crystallographic structures of the as-obtained NiCo nanowires were characterized by XRD. A meaningful result is that the different diffraction pattern for different potential has been obtained. The diffraction peaks of the template are observed under -0.8V. When the deposition potential is -1.0V, cubic Ni(111) and Co(304) – Ni(200) has also been indicated. However, only a very strong Ni (111) peak can be seen in the XRD spectrum of the NiCo nanowires deposited under a voltage of -1.2V, which means that the NiCo nanowires exhibit a highly preferential orientation. When the deposited voltage changes to -1.4V, the Co(100) peak can be seen, indicating the formation of NiCo alloying phase with a single-crystal structure. The NiCo nanowires show the same diffraction peaks deposited under the potential of -1.6V and -1.8V, and from the XRD figure, we can see that the

intensity of the Ni(111) peak increase and then decrease with increasing deposition potential. In a word, the different orientation of NiCo nanowires in different potentials have been indicated.

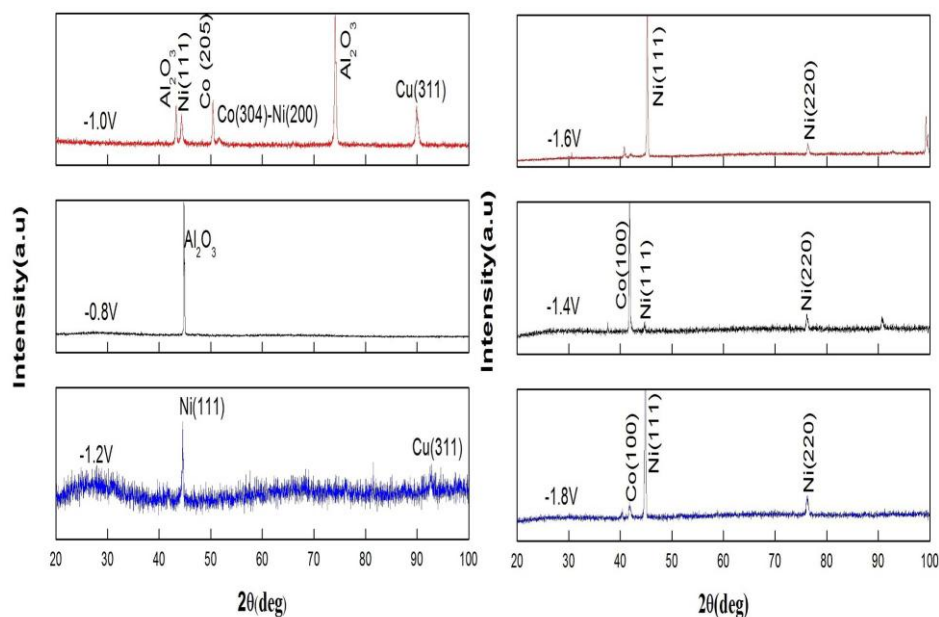


Figure 4. XRD patterns of NiCo nanowires with varying potentials

The dependence of the magnetic properties of NiCo nanowires, such as coercivity and saturation magnetization, related to the electrodeposition potential is shown in Fig.5. Magnetic properties of NiCo nanowires embedded in an AAO are closely related to the microstructure. It is well known that reducing the nanowire diameter can improve the coercivity of the nanowires. In addition, the coercivity of the nanowires can be enhanced by increasing their length. From the results, it is clear that prepared under more positive deposition potential (-0.8 V and -1.0 V), the magnetic properties of NiCo nanowires present poor soft magnetic properties (M_s (-0.8V) = 81 emu/cm²) as shown in Fig. 5(a), but the coercivity of NiCo nanowire is 502 Oe, comparative XRD graph that the growth of the nanowires are slow because of no metal peak. It is noteworthy that the saturation magnetization of NiCo nanowires was improved when the deposition potential is more negative, but the coercivity doesn't show a clear downward trend. In Fig. 5, when the potential is -1.6V, the coercivity is only 103 Oe, the nanowires have relatively good soft magnetic properties when the deposition voltage was -1.6V. It can be concluded that the magnetic properties are related to the nanowires structure. The structure of nanowires is also affected by the deposition potential. NiCo nanowires exhibit different magnetization because of different diffraction peaks under different potentials.

Fig. 6 shows the horizontal and perpendicular hysteresis loops of NiCo nanowires under different deposition potential. The saturation magnetization of horizontal and perpendicular direction is very different under the deposition potential of -1.0V and -1.2V and is equivalent under others deposition potentials conditions. When the deposition potential is -1.0V, -1.4V, -1.6V, -1.8V, different coercivities of NiCo magnetic nanowires in horizontal and perpendicular conditions are observed.

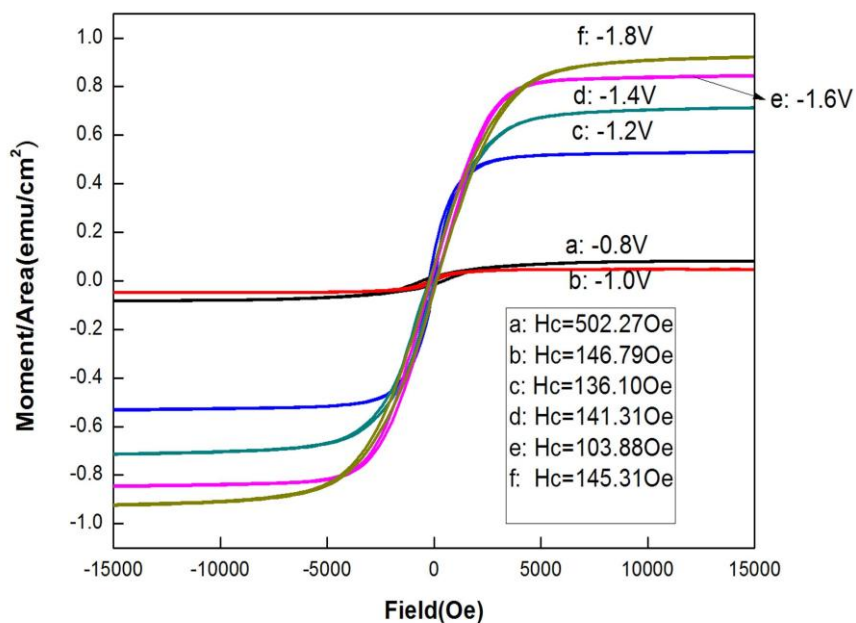


Figure 5. Magnetic hysteresis loops of the NiCo alloy nanowires with different potential

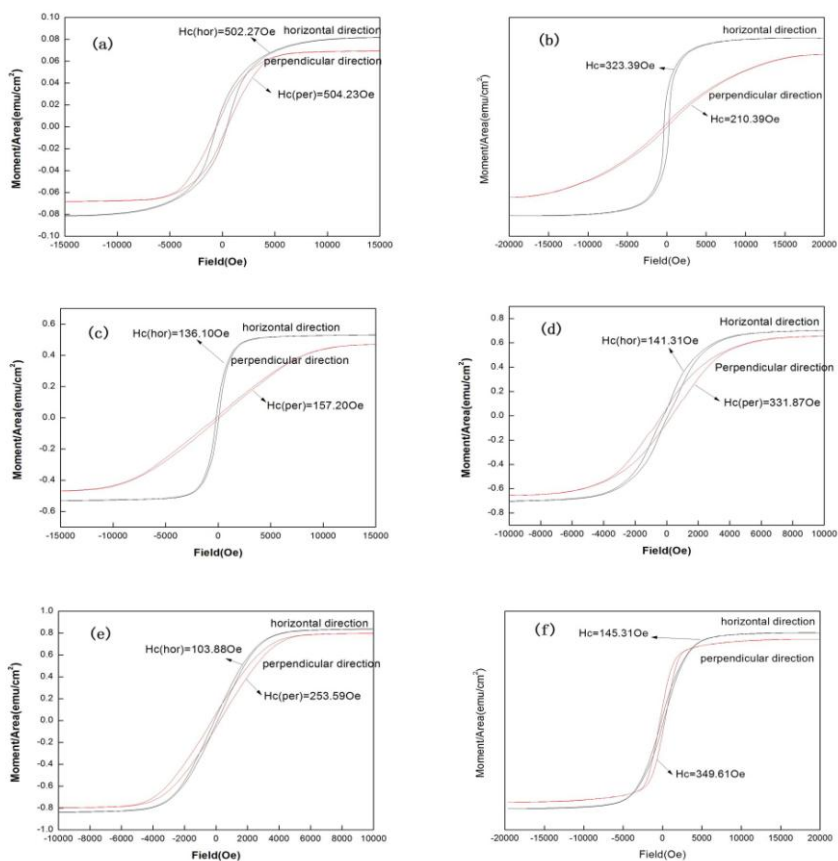


Figure 6. horizontal and perpendicular magnetic hysteresis loops of the NiCo alloy nanowires with different potentials: (a). -0.8V; (b). -1.0V; (c). -1.2V; (d). -1.4V; (e). -1.6V; (f). -1.8V

The results demonstrate that NiCo nanowires have hysteresis anisotropy in potentials (-1.0V, -1.4V, -1.6V, -1.8V). Comparison of Figures 4 and 6, we know that when the deposition voltages are -1.0V, -1.4V, -1.6V, -1.8V, there are some metals diffraction peak, indicating that the nanowires were synthesized, and the crystal structure of nanowires is different, It should be noted that the different structure that can help to improve the magnetic properties of NiCo nanowires[15], and For NiCo nanowires similar magnetic curves were observed by applying parallel or perpendicular magnetic fields, which reveal magnetic anisotropy as a function of their aspect ratio[16].

4. CONCLUSION

Highly ordered NiCo nanowires have successfully been fabricated by DC electrodeposition. The structure and magnetic properties of NiCo nanowires have been investigated. The results have showed that the as-obtained nanowires exhibit a diameter of about 90nm. The crystalline structure of NiCo nanowires depends on the voltages during the DC deposition, the different diffraction peaks of NiCo nanowires appear with potential of -0.8V to -1.8V. The magnetic properties of NiCo nanowires are as the function of the NiCo structure. When the potential is -0.8V, the coercivity of NiCo nanowire is 502Oe. The minimum value of coercivities to the nanowire is 103 Oe, when the voltage is -1.6V. NiCo nanowires show hysteresis anisotropy under the electrodeposition potential of -1.0V, -1.4V, -1.6V and -1.8V, the result was related to the XRD result which showed the different peaks. In summary, the morphology and magnetic properties are affected by the deposited potential.

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