

**ORIGINAL RESEARCH PAPER**

## Investigations of Magnetic Properties Through Electrodeposition Current and Controlled Cu Content in Pulse Electrodeposited CoFeCu Nanowires

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**Abstract**

CoFeCu nanowires were deposited by pulsed electrodeposition technique into the porous alumina templates by a two-step mild anodization technique, using the single-bath method. The electrodeposition was performed in a constant electrolyte while Cu constant was controlled by electrodeposition current. The electrodeposition current was 3.5, 4.25, 5 and 6 mA. The effect of electrodeposition current and annealing on the magnetic behavior of the nanowires was investigated. Nanowires were fabricated with 30nm diameter and 100nm inter-pore distance with both bcc-CoFe and fcc-Cu phases. With increasing the electrodeposition current the Cu content decrease and the coercivity and magnetization increase up to its optimum value, then decrease. Annealing improved the coercivity, maximum coercivity was obtained for sample fabricated at 5 mA current. After annealing the magnetization decrease for all samples. The X-ray diffraction pattern of the sample at electrodeposition current 3.5 mA after annealed indicates that Cu and CoFe phases separately was formed and separate peak related to CoFeCu alloy structure is not seen.

### 1. INTRODUCTION

Nanowire arrays have received much attention due to their potential for increased area density magnetic media and gas sensors [1-2]. Researchers are recently centralized on binary and ternary magnetic alloys [3-4], particularly magnetic-non magnetic alloys such as Cu[5], Pb[6], Pt[7,8].

CoFe nanowires have recently received more attention [9]. Adding non-magnetic elements (such as Zn [10], P[11], B[12] and Pb[13]) to magnetic nanowires is a common method to control their magnetic properties. In the present work CoFeCu alloy nanowires were ac-pulse electrodeposited into the alumina template. The influence of

electrodeposition current density and the annealing on the magnetic properties of nanowires were investigated.

## 2. Experimental procedure

The AAO templates were prepared by a two steps anodization process [14]. Initially 0.3 mm thick high purity aluminum foils (99.999%) were electropolished in a 4:1 volume mixture of ethanol and perchloric acid. Then the foils were anodized in a 0.3 M oxalic acid solution at 17°C for 5 h at 40 V. The anodized foils were immersed in a solution composed of 0.5 M phosphoric acid and 0.2M chromic acid at 60°C for 10 h to remove the anodized layer. The samples were reanodized for 3h at the first step. To promote thinning of the barrier layer, following the second anodization step, voltage was systematically reduced to 12 V.

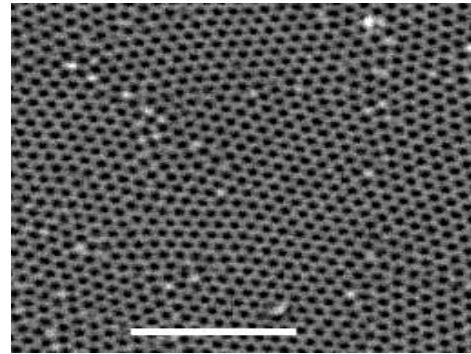
The ac-pulse electrodeposition method was used to deposit CoFeCu nanowires into the nanopores. The electrodeposition current was 3.5, 4.25, 5, 6 mA and the off-time was 100 ms and the reduction and oxidation times were 2.4 ms. A sin waveform with 13/12 V reduction/oxidation voltage was used during the electrodeposition process. The electrolyte was a solution composed of 0.15M  $\text{Co} \cdot \text{SO}_4 \cdot 7\text{H}_2\text{O}$ , 0.15M  $\text{Fe} \cdot \text{SO}_4 \cdot 7\text{H}_2\text{O}$ , 0.01M  $\text{Cu} \cdot \text{SO}_4 \cdot 5\text{H}_2\text{O}$ , 40 g/l  $\text{H}_3\text{BO}_3$  and 1 g/l  $\text{C}_6\text{H}_8\text{O}_6$ .

The pH value of electrolyte solution was 3 and the electrolyte temperature was 30°C. For investigate the surface morphology of the samples atomic force microscopy (AFM) was employed. The structure and composition of CoFeCu nanowire arrays were investigated by X-ray diffraction pattern (XRD) and X-ray fluorescence (XRF). A vibrating sample magnetometer (VSM) at room temperature was employed to study the magnetic properties of the as prepared and annealed samples

at 570°C in a mixture of 15% hydrogen and 85% argon gases for 30 min.

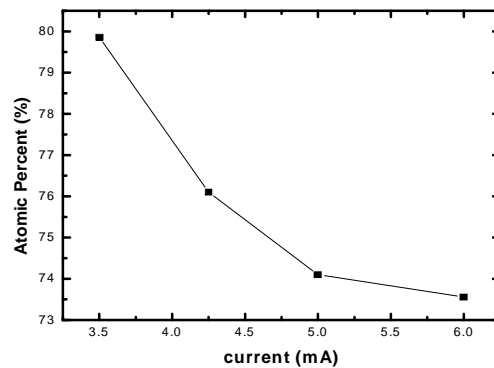
## 3. Results and discussion

A top view AFM image of the nanopore arrays prepared by the two step anodization method was shown in Fig.1. The inter-pore distance and pore diameter are approximately 100nm and 30 nm, respectively.



**Fig. 1.** A top view AFM image of the nanopore arrays prepared by two step anodization method, the scan size is 1 $\mu\text{m}$ .

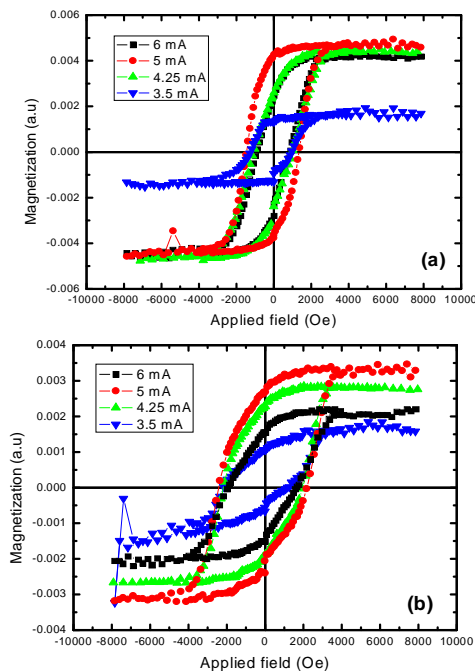
The result of XRF analysis of the CoFeCu nanowire arrays prepared by different electrodeposition currents is shown in Fig.2. It is found that deposition rate of the Cu and CoFe is not the same.



**Fig. 2.** Cu atomic percentage of CoFeCu nanowires arrays as a function of current

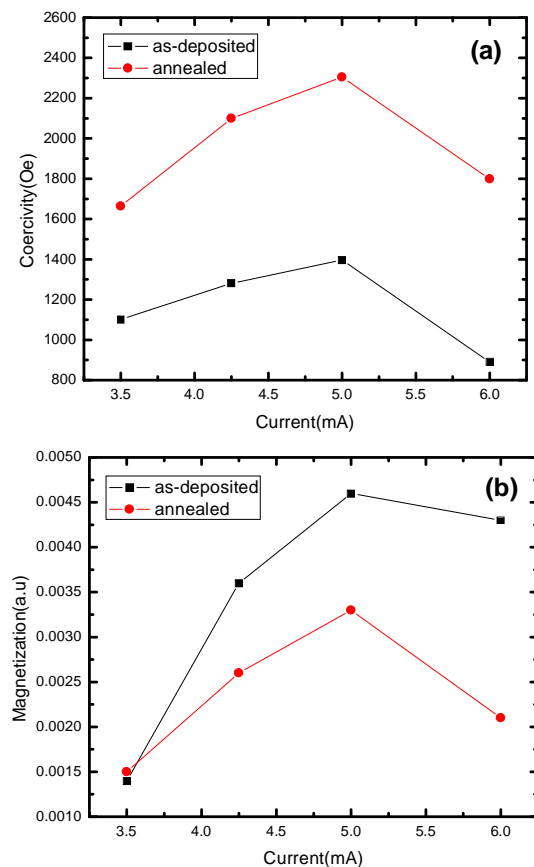
Since same electrolyte was used to deposited all the samples, decreasing of Cu content with electrodeposition current may be related to effective deposition competition between Cu and Co, Fe atoms, It seems that replacement of magnetic Co and Fe atoms with non-magnetic Cu atoms has occurred during the off-time between pulses through electroless process. However, the rate of this replacement decrease with increasing of electrodeposition current. Based on this point we can control Cu content of CoFeCu alloy nanowires by controlling the electrodeposition current.

Hysteresis loops of alloy nanowire were obtained with external magnetic field applied parallel to the wires axis at room temperature. Fig.3 shown the hysteresis loops of the both as prepared and annealed samples.



**Fig. 3.** Hysteresis loops of a)as-prepared and b) annealed CoFeCu nanowire arrays prepared at different electrodeposition currents.

The coercivity and saturation magnetization of as prepared and annealed samples as a function of electrodeposition current is shown in Fig.4a and Fig.4b, respectively. As shown coercivity and magnetization of samples initially enhances and then reduces. Reduction of magnetization with increasing of the current also confirms XRF result. After annealing, magnetization of the nanowires prepared at 5 and 6 mA current is seen to decrease down 28 % and 51% respectively and coercivity increases from 1102Oe to 1664Oe and from 1396 Oe to 2304 Oe for the sample synthesized at 3.5 and 5 mA current, respectively.



**Fig.4.** a) Coercivity b) magnetization of as-deposited and annealed samples as a function of electrodeposition current.

In nanowires with higher Cu content, the magnetic atoms were individually distributed between non-magnetic Cu atoms and could not show their real contribution in the magnetization. Formation of magnetic CoFe clusters during the annealing enhances the coercivity of these samples. The decrease in magnetization of annealed nanowire arrays may be caused by the changes of nanowires structure in the annealing process. It may be said that decrease of magnetization is related to the entering Cu atoms to the CoFe cluster during the annealing process.

The X-ray diffraction pattern of the prepared sample at electrodeposition current 3.5 mA after annealed (Fig.5) exhibit the polycrystalline structure. Three peaks related to Cu(111), CoFe(100) and Cu(200) have been appeared at 43.55°, 45.04° and 50.64° respectively. The X-ray diffraction pattern indicates that Cu and CoFe phases separately was formed and separate peak related to CoFeCu alloy structure is not seen.

#### 4. Conclusion

CoFeCu nanowires with different Cu content were ac-pulse electrodeposited through variation of electrodeposition current. The obtained results listed as follows:

- The Cu non-magnetic element in CoFeCu alloy nanowires decrease with increase of the current.
- Increasing the electrodeposition current causes increase of coercivity up to its optimum value, then decreases.
- Annealing led to increase the coercivity and decrease the magnetization.
- X-ray analysis revealed formation of CoFeCu solid solution with separate Cu and CoFe phases.

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#### References:

- [1] J.I. Martin, J. Nogues, K. Liu, J.L. Vincent, I.K. Schuller, *J. Magn. Mater.* 256, 449 (2003)
- [2] M.S. Sander, A.L. Prieto, R. Gronsky, T. Sands, A.M. Stacy, *Adv. Mater.* 14, 665 (2002)
- [3] J.X. Xu, K.Y. Wang, Y. Xu, *Chemistry Letters* 36 (2007) 868-875.
- [4] M.B. Jeong, S. Martin, M. Martin, *Journal of Physical Chemistry C* 112 (2008) 2252-2260.
- [5] X. Liu, J. Zhao, Y. Li, S. Xu, Z. Zhu, J. Chen, G. Wu, *Chem. Lett.* 36 (2007) 166-173.
- [6] G.B. Ji, W. Chen, S.L. Tang, B.X. Gu, Z. Li, Y.W. Du, *Solid State Commun.* 130 (2004) 541- 550.
- [7] S. Shamailaa, R. Sharif, S. Riaz, M. Ma, M. Khaleeq-ur-Rahmanb, X.F. Han, J. *Magn.Magn.Mater.*320 (2008) 1803-1810.
- [8] Y. Dahmane, L. Cagnon, J. Voiron, S. Pairis, M. Bacia, L. Ortega, N. Benbrahim, A. Kadri, *J. Phys. D: Appl. Phys.* 39 (2006) 4523-4530.
- [9] M. Ciureanu, F. Beron, L. Clime, P. Ciureanu, A. Yelon, T.A. Ovari, R.W. Cochrane, F. Normandin, T. Veres, *Electrochim. Acta* 50 (2005) 4487.
- [10] J.M. Yang, Y.T. Hsieh, D.X. Zhuang, I.W. Sun, *Electrochem. Commun.* 13 (2011) 1178.
- [11] D.S. Xue, J.L. Fu, H.G. Shi, *J. Magn. Mater.* 308 (2007) 1.
- [12] R. Sharif, X.Q. Zhang, S. Shamaila, S. Riaz, L.X. Jiang, X.F. Han, *J. Magn. Mater.* 310 (2007) e830.
- [13] R.L. Wang, S.L. Tang, Y.G. Shi, X.L. Fei, B. Nie, Y.W. Du, *J. Appl. Phys* 103 (2008) 07D507.

- [14] M. AlmasiKashi, A. Ramazani, A. Khayyatian, J. Phys. D 39 (2006) 4130.