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Investigations of Microstructures and Magnetic Properties through Off-time between Pulses and Controlled Cu Content in Pulse Electrodeposited NiCu Nanowires

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Abstract

NiCu alloy nanowires arrays were embedded into the anodic aluminum oxide (AAO) template by ac-pulse electrodeposition. Different off-time were used in electrolyte with constant concentration of Ni and Cu and acidity of 3. The effect of deposition parameters on alloy contents was investigated by studying the microstructure and magnetic properties of as-deposited NiCu alloy nanowires. Atomic force microscopy, x-ray analysis were employed to investigate the morphology and microstructure of prepared sample. Vibrating sample magnetometer was also used in order to study the magnetic properties of nanowires array. The obtained results revealed, with increase in off-time, Cu non-magnetic element content increases through electroless process.

1. Introduction

Nanowire arrays are attractive for their potential applications in high density recording media [1], giant magneto resistance (GMR) [2], sensor devices [3], photonic crystals [4]. Researchers are recently focused on binary and ternary magnetic alloys [5-6], especially magnetic-nonmagnetic alloys. The nonmagnetic element added in magnetic nanowires able to control the magnetic properties of the nanowire arrays. Some examples of non-magnetic elements have been added in the magnetic nanowire arrays such as Cu[7], Pb[8], Pt[9,10].

Among different methods used to fabricate nanowires, self-ordered anodized aluminum oxide (AAO), because of it is economical, simple and ability to controlling the interpore distances, length and pore diameter of nanopores were employes.

The ac - pulse deposition technique yielded uniformity of porefilling in comparison to the continuous ac electrodeposition.

In the present work, NiCu nanowires embedded in porous aluminum oxide template were fabricated using ac pulse electrodeposition technique. The effect of off-time between pulses on the microstructure and magnetic properties of nanowires were investigated.

2. Experiments

Anodic aluminum oxide (AAO) template were prepared by a two steps anodization process. Initially, the high purity aluminum foils (99/999%) were electropolished in 4:1 mixture solution of ethanol and perchloric acid. To obtain highly ordered pores a two-step anodization process was employed. In the first step, the foils were anodized in 0.3 M oxalic acid solution at 40 V for 10 h and at 17 °C temperature. The anodized foils were immersed in a solution composed of 0.2 M chromic and 0.5 M phosphoric acid for 10 h at 60 °C to remove the anodized layer.

The samples were reanodized for 4 h at the same conditions as the first step.

To promote thinning of the barrier layer, the anodization voltage was systematically reduced to 10 V.

Nanowires were prepared by solution composed of 0.3 M $NiSO_4.7H_2O$, and 0.005 M $CuSO_4.5H_2O$ and 45 g/l H_3BO_4. The ac pulse electrodeposition technique was performed to deposit nanowires into the nanopores. Electrodeposition was carried out in condition of a sine waveform with 11/10 V reduction/oxidation voltage and with same reduction/oxidation time of 5 ms. Off-time between pulses were 2.5, 10, 20 and 40 ms. The electrolyte temperature was 30 °C. Also, the pH value of electrolyte solution was 3. The structure and composition of NiCu nanowires arrays were investigated by X-ray diffraction analysis and X-ray fluorescence (XRF).The magnetic properties were measured by vibrating sample magnetometer (VSM) at room temperature. Atomic force microscopy (AFM) was employed to investigate the surface morphology of the samples.

3. Results and discussion

3.1. Microstructure investigation

A top view AFM image of the nanopore arrays fabricated by the two step anodization method is displayed in fig (1). According to this figure, the nanopore hexagonally arranged with diameter and interpore distance of approximately 30 and 100 nm respectively, can be seen.

The samples were prepared with different off-time in electrolyte solution containing 0.3 M nickel sulfate and 0.005 M copper sulfate.

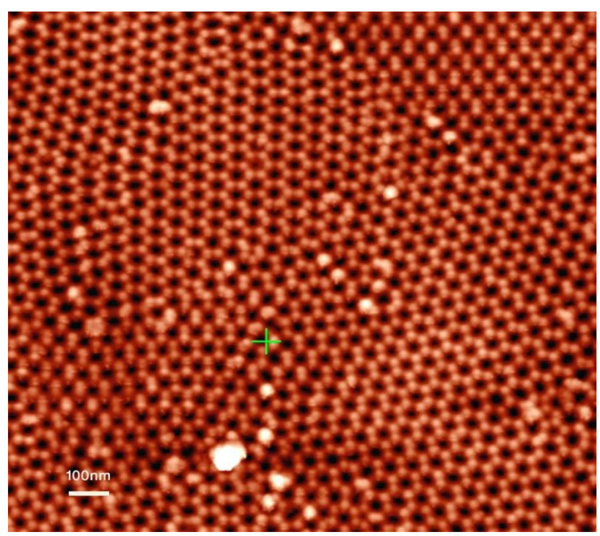

Fig.1. A top view AFM image of the nanopore arrays fabricated by using of the two step anodization method.

The result of XRF analysis of the NiCu nanowire arrays fabricated by various off-times is displayed in fig (2).The XRF analysis evinced that the electrodeposition rate of Cu and Ni ions was not the same.

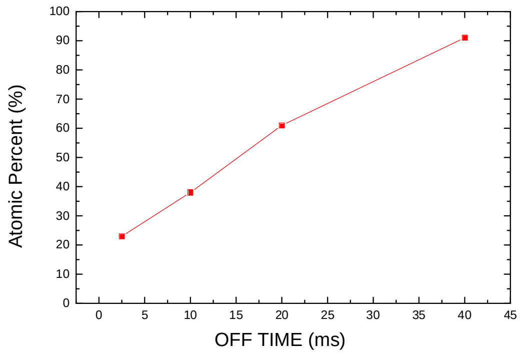

Fig. 2. Cu atomic percentage of NiCu nanowires arrays as a function of off-time.

As shown in fig (2), the atomic percentage of Cu in fabricated nanowires has been enhanced from 23% to 91% when the off-time increased from 2.5 to 40 ms. Really, at 40 ms off-time the prepared nanowire are Cu-rich. It can be said that, increasing the off-time lead to enhancement of Cu content in NiCu alloy nanowires.

With increase in the off-time copper atoms considering their higher standard potential (E_0 = 0.3 V) take the opportunity to replace nickel atoms existent in crystalline structure, (standard potential of Ni 1.4 V), through electroless process. The more increase in off-time, the more Cu atoms are replaced with Ni atoms.

Of course this result is in accordance with the results of EDS analysis for deposition of CoCu nanowires arrays [11, 12]. It is observed that increase in off-time leads to increase in Cu content of deposited nanowires to about more than 60%.

The above results are consistent with the x-ray diffraction patterns indicated in fig (3).

The x-ray diffraction pattern shows that, Ni and Cu phases separately was formed and separate peak related to NiCu alloy structure is not seen.

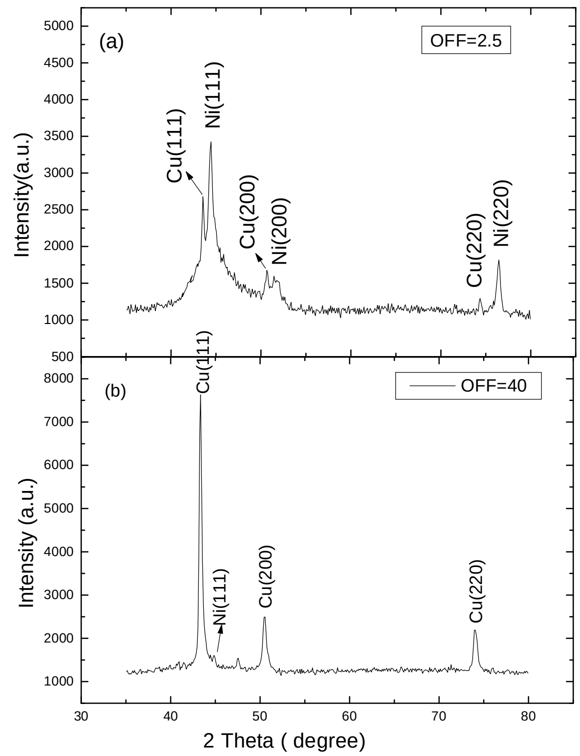

Fig. 3. X-ray diffraction patterns of prepared NiCu nanowires with a)2.5 ms and b)40 ms off-times.

As shown in fig (3), manifestly, the Cu peaks intensity has increased with increasing the off-time from 2.5 to 40 ms (due to electroless). At 2.5 ms off-time three peaks related to (111), (200) and (220) of Ni face centered cubic structure have been appeared at 44.5˚, 51.83˚ and 76.4˚ respectively. But with increase in off-time to 40ms, only one (111) Ni peak was observed around 44.37˚ and majority of peaks are dependent to Cu structure.

Of course, these results were anticipated to considering XRF analysis. On the other hand, increasing off-time causes to more Ni atoms are replaced by Cu atoms through electroless process.

3.2. Magnetic analysis

Hysteresis loop of the as-deposited NiCu alloy nanowires synthesized by various off-time with 0.005M copper sulfate concentration, are displayed in fig(4). Magnetization measurements were carried out at room temperature, with applying external magnetic field parallel to long-axis of the nanowires.

As shown in fig(4), the magnetic properties (coercivity and saturation magnetization values) were decreased, with increase the off-time from 2.5 to 40 ms.

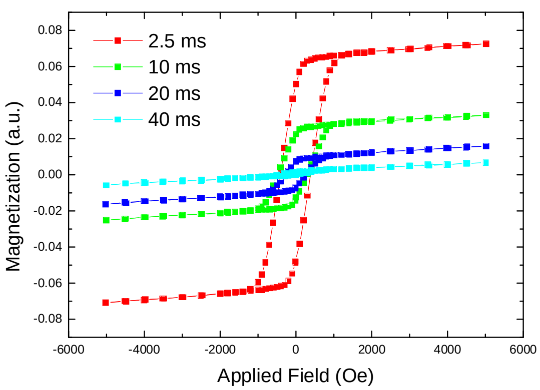

Fig. 4. Hysteresis loops of the as-deposited samples prepared with different off-times.

Fig(5) demonstrates coercivity and saturation magnetization of the as-deposited NiCu nanowires as a function of off-time. As shown in this figure, magnetization of the as-deposited samples rebated from 66 at 2.5 ms to negligible content 1 at 40 ms off-time. This problem demonstrates the influence of Cu non-magnetic element in nanowires structure, (see fig(3)).

It is reported [11, 12] that increasing the off-time reducesthe saturation magnetization ,because of electroless process, in CoCu nanowires arrays.

The corcivity of these samples, decreased from 394.5 Oe value at 2.5 ms to 305 Oe at 40 ms off-time. The only exception is seen for the 10 ms, off-time.

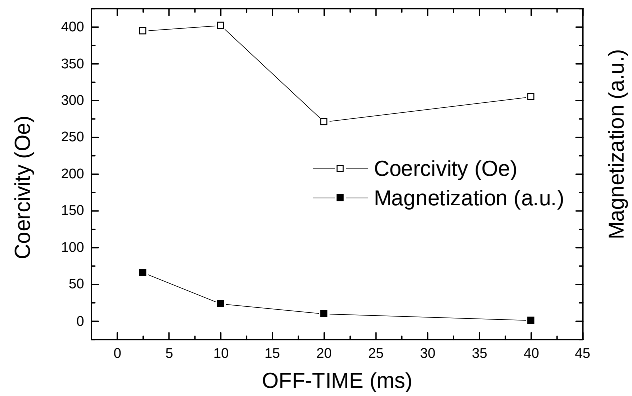

Fig. 5. Coercivity and magnetization of as-deposited samples as a function of off-times.

It is observed that, compatible with obtained results of XRF analysis, increasing off-time increased the Cu content of nanowires. This in turn degrades the magnetic properties. On the other hand, increasing off-times causes more replacing the Ni with Cu atoms through electroless process.

It is also observed that increase in off-time, decrease the coercivity of CoCu nanowires arrays in electrolyte containing 0.025M CuSO4 concentration [12].

In justification of increase of coercivity at 10ms off-time; it can be said that, added a small amount of Cu in structure of Ni improves the magnetic property of nanowire. This was also reported for CoCu.

4. Conclusion

NiCu nanowire arrays were fabricated by ac pulse electrodeposition with different off-times. The investigations was focused on the effect of off-time on the composition, microstructure and magnetic properties of NiCu alloy nanowires, the obtained results enable us to reach the following conclusions:

a) Increasing the off-times causes to increase of Cu non-magnetic element in NiCu alloy nanowires.

b) Separately Ni and Cu fcc phases were formed in synthesized samples.

c) The Cu peaks intensity has increased with increasing of off-time.

d) The corcivity and magnetization in as-deposited NiCu nanowires were decreased, with increase the off-time.

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References

[1] H. Oshima, H. Kikuchi, H. Nakao, T. Morikawa, K. Matsumoto, K. Nishio, H. Masuda, K. Itho, Japanese Journal of Applied Physics 44 (2005) L1355.

[2] I.Bakonyi,L.Pe´ter, Progressin Materials Science 55 (2010) 107-112.

[3] E.C. Walter, R.M. Penner, H. Liu, K.H. Ng, M.P. Zach, F. Favier, Surface and Interface Analysis 34 (2002) 409-416.

[4] A. Chelnokov, S. David, K. Wang, F. Marty, J.M. Lourtioz, IEEE Journal of Selected Topics in Quantum Electronics 8 (2002) 919-925.

[5] J.X. Xu, K.Y. Wang, Y. Xu, Chemistry Letters 36 (2007) 868-875.

[6] M.B. Jeong, S. Martin, M. Martin, Journal of Physical Chemistry C 112 (2008) 2252-2260.

[7] X. Liu, J. Zhao, Y. Li, S. Xu, Z. Zhu, J. Chen, G. Wu, Chem. Lett. 36 (2007) 166-173.

[8] G.B. Ji, W. Chen, S.L. Tang, B.X. Gu, Z. Li, Y.W. Du, Solid State Commun. 130 (2004) 541-550.

[9] S. Shamailaa, R. Sharif, S. Riaz, M. Ma, M. Khaleeq-ur-Rahmanb, X.F. Han, J. Magn.Magn.Mater.320 (2008) 1803-1810.

[10] 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.

[11] M. Almasi Kashi, A. Ramazani, F. AdelniaNajafabadi, Z. Heydari, J. Applied Surface Science. 257 (2011) 9347-9355.

[12] M. Almasi Kashi, A. Ramazani, F. AdelniaNajafabadi, Journal of Alloys And Compounds. 540 (2012) 133-139.