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Magnetic properties improvement through off time between pulses and annealing in pulse electrodeposited CoZn nanowires

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ABSTRACT

CoZn alloy nanowire arrays embedded in anodic aluminum oxide (AAO) template were fabricated by alternative current (ac) pulse electrodeposition. Various off times between pulses in an electrolyte with constant concentration of Co^{+2} and Zn^{+2} and acidity of 4 were employed. The effect of deposition parameters on the alloy contents, microstructures and magnetic properties of Co_xZn_{1-x} nanowires were studied. It is shown that, Co content increased by increasing the off time between pulses. This phenomenon enables us to fabricate Zn and Co-rich nanowires by adjusting the off time during the deposition procedure. Increasing the off time more than 200 ms increased the coercivity and squareness of CoZn nanowire arrays. A significant increase in the coercivity of CoZn nanowires was observed after annealing which was varied for the samples fabricated with different electrodeposition conditions. A coercivity of 1785 Oe was obtained for the annealed sample (a sample fabricated with 50 ms off time) from initially 240 Oe.

1. Introduction

Conductor and semiconductor nanowires embedded in nanoporous anodic aluminum oxide (AAO) have attracted great interest during last decade. Thermal, mechanical and chemical properties along with specific geometries and easy fabrication of nanowires into the aluminum oxide template are the main reasons for AAO to be a proper template preparing magnetic recording media [1,2]. Another reason using AAO template is its morphology which exhibits a lot of homogeneous parallel pores growing perpendicular to the surface with a narrow distribution of diameter so that their length could be well controlled in a wide range of distances. Both direct and alternative currents were performed to electrodeposit nanowires into the porous alumina. Deposition into the pores using direct current (dc) electrodeposition method has proven to be a particularly powerful technique, enabling substantial control over composition and crystallinity [3,4] and easy access to compositional modulation along the wire lengths [5]. However, none of the dc techniques reported to date are amenable to industrial scale processing because of the laborious preprocessing that must be performed on the AAO template before deposition. In contrast, alternative current (ac) deposition technique requires fewer processing steps and is more amenable to scale-up but currently provides far less control over the structure of the material deposited. In general, ac electrodeposition through the barrier layer is a complicated process which depends on deposition conditions such as electrolyte concentration, composition and temperature [6], as well as deposition voltage, frequency and waveform (sine, square and triangle) [7,8]. Fabrication of alloy nanowires using ac and pulse electrodeposition techniques is more complicated than pure element nanowires such as Cu, Co, Fe and Ni [8–11]. Therefore it is valuable to investigate the effects of electrodeposition parameters on the microstructure and magnetic properties of magnetic alloys nanowires. Among magnetic nanowires, magnetic and nonmagnetic Co based alloys have been more interested because of its uniaxial crystal structure. There have been numerous reports studying the microstructures and magnetic properties of Co based alloys such as CoFe [12], CoNi [13], CoCu [14], CoPt [15,16], CoPd [17,18], CoPb [19,20] and CoZn [21,22].

In the present work in a constant electrolyte, CoZn nanowires with various Zn contents were synthesized by varying the off time between pulses of the ac pulse electrodeposition voltage. Performing pulse electrodeposition in a certain electrolyte concentration enables us to fabricate CoZn alloy nanowires with various compositions. The effect of pulse electrodeposition conditions and annealing on the microstructure and magnetic properties of nanowires were investigated.

2. Experiments

The AAO templates have been prepared by a two step anodization process. Highly pure aluminum foils of 0.3 mm thickness were electropolished in a 1:4 volume mixture of perchloric acid and ethanol. The foils were then anodized in 0.3 M oxalic acid solution at 17 °C for 10 h at 40 V. Subsequently, the anodized foils were

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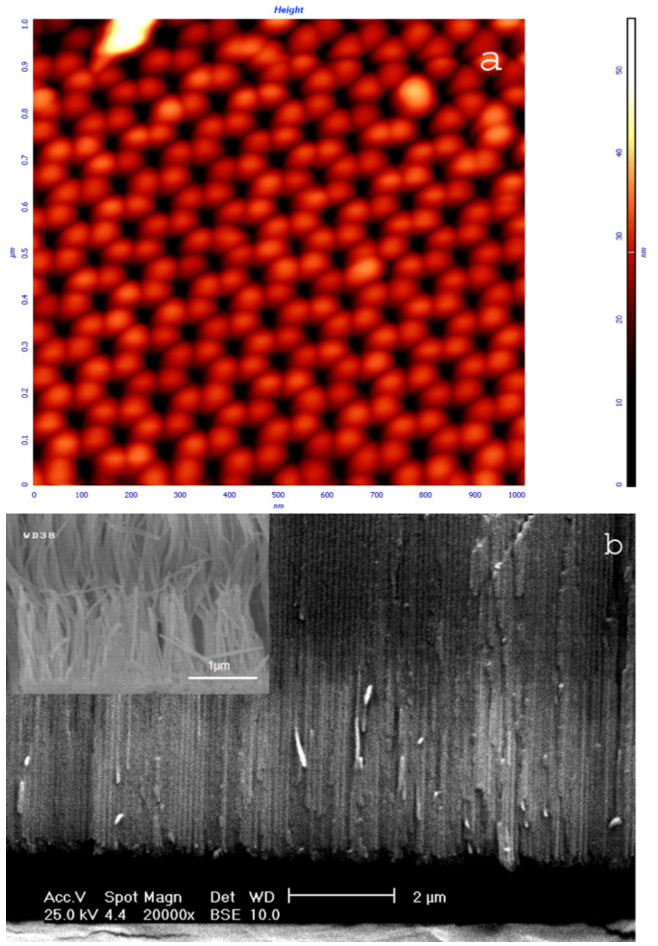

Fig. 1. (a) A top view AFM image of the nanopore arrays prepared by the two step anodization method for 2 h and (b) a cross section SEM micrograph of $Co_{0.8}Zn_{0.2}$ nanowire arrays prepared with an effective electrodeposition time of 1 min. A cross section view of nanowires after removing of alumina template is inserted.

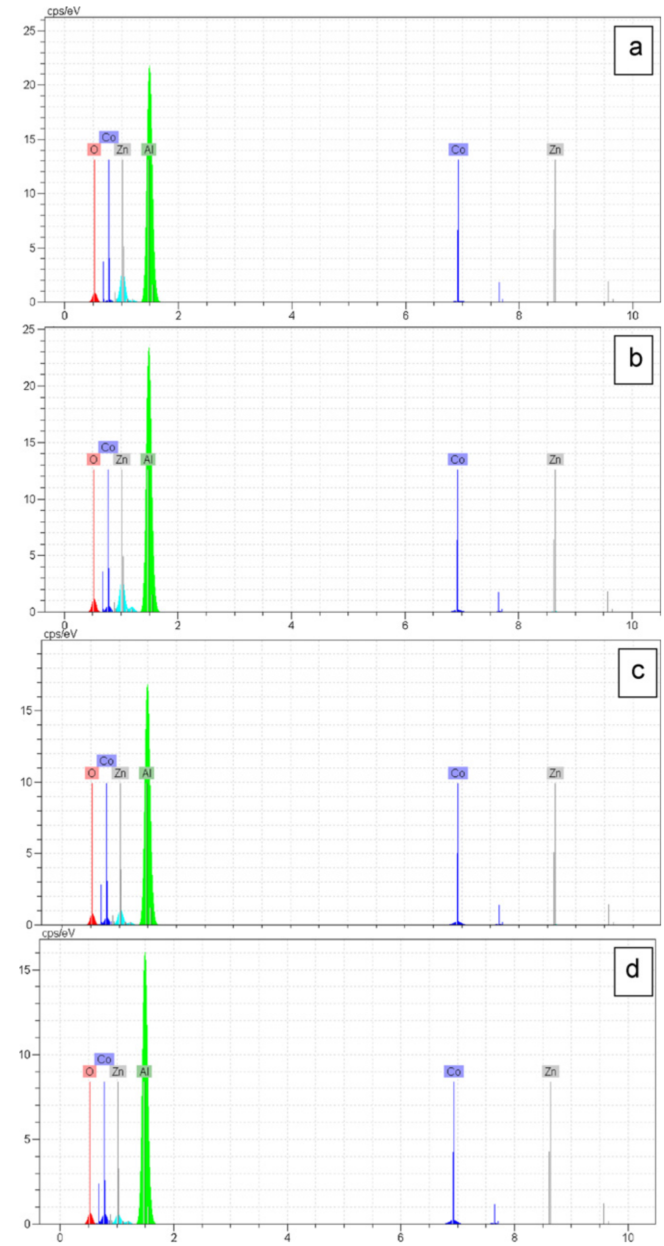

Fig. 2. EDS patterns of the CoZn nanowire arrays fabricated by (a) 10, (b) 50, (c) 400, (d) 600 ms, off-time between pulses.

immersed in a solution composed of 0.2 M chromic and 0.5 M phosphoric acid at 60 °C for 10 h to remove the anodized layer. The foils were then anodized, by identical parameters as the first step for 2 h. Following the second anodization step, voltage was reduced systematically to promote thinning of the barrier layer. The voltage was initially reduced by a rate of $0.064\,V\,s^{-1}$ to 20 V and then $0.033\,V\,s^{-1}$ to 12 V and ultimately anodization continued in the last voltage for 1 min in order to barrier layer reaches to equilibrium.

The ac pulse electrodeposition technique in a simple electrochemical cell with 2 electrodes was performed to deposit nanowires into the nanopores. Reduction and oxidation times were 5 ms and the off time between pulses was 10, 20, 50, 100, 200, 400 and 600 ms. A sine waveform with 18/18 V reduction/oxidation voltage was employed during the electrodeposition process. A solution composed of 0.3 M $CoSO_4{\cdot}7H_2O$, 0.06 M $ZnSO_4{\cdot}7H_2O$, $45\,g\,l^{-1}$ H_3BO_3 was used as electrolyte. The pH value of electrolyte solution was initially 3.3–3.5, which increased to 4 by adding $NaHCO_3$. The effective electrodeposition time (the total electrodeposition time minus entire off times between pulses) was 60 s.

The structure and composition of the arrays of CoZn nanowires were studied by X-ray diffraction pattern and electron dispersive spectroscopy (EDS). The magnetic properties were measured by alternating gradient force magnetometer (AGFM) at room temperature. Scanning electron microscope (SEM) and atomic force microscopy (AFM) were employed to investigate the surface morphology of the samples.

3. Results and discussions

Fig. 1(a) shows a typical AFM top view image of the nanopore arrays prepared by the two step anodization method. Relatively perfect hexagonally arranged nanopores with 30 nm diameter and 100 nm interpore distances can be seen. Fig. 1(b) shows a typical SEM micrograph of the cross section of $Co_{0.8}Zn_{0.2}$ nanowire arrays prepared with an effective electrodeposition time of 1 min. The wires have an average length of 3.5 µm. The nanowires are parallel to each other through the entire pores. For more detail a cross section view of nanowires after removing of alumina template is also inserted in Fig. 1(b).

Fig. 2 shows EDS patterns of the CoZn nanowire arrays fabricated by various off-time between pulses. The oxygen and aluminum peaks are related to the alumina template. The Co content of CoZn nanowire arrays is tabulated in Table 1. It is found that Co content in fabricated nanowires has been enhanced from 58.2% at 10 ms off time up to 80% at 600 ms off time. Consequently, it may be said

Table 1
The Co content of CoZn nanowire arrays as a function of off time between the pulses.

Off time (ms)	10	50	400	600
Co Content (at.%)	58.2	61	73.6	80

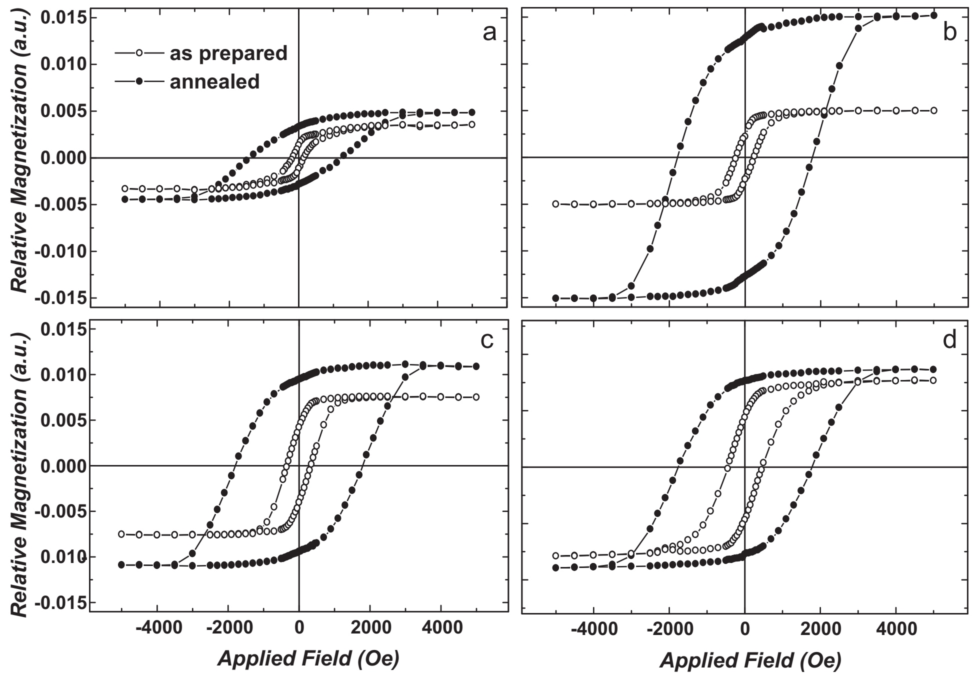

Fig. 3. Hysteresis loops of both the as prepared samples and annealed ones synthesized at (a) 10, (b) 50, (c) 400 and (d) 600 ms off times.

that increasing the off time results in enhancement of Co content in CoZn alloy nanowires. Using electrolyte with same concentration of Co and Zn ions and applying same reduction voltage for all the samples, it was expected the fabricated CoZn nanowires show same alloy compositions but this fact was not experimentally confirmed. It seems by applying ac pulse in an electrochemical cell, metallic zinc and cobalt ions reduce in competing with each other,

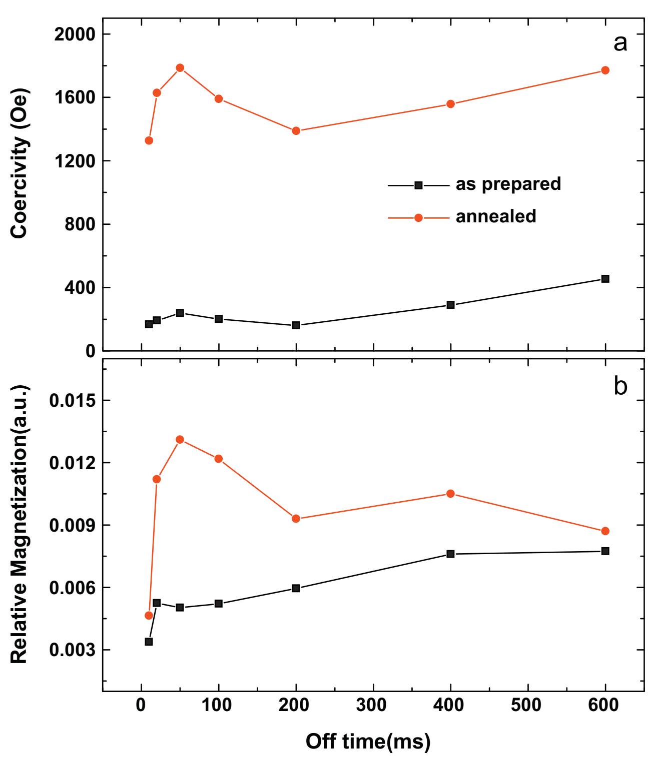

Fig. 4. (a) Coercivity and (b) magnetization of prepared and annealed samples, as a function of off time between pulses, with applied field parallel to the wire's axis.

but during the off time cobalt atoms considering their higher standard potential ($E_0 = -0.28$ V) take the opportunity to replace zinc atoms (with standard potential of −0.76). By increasing off time, more numbers of Zn atoms are replaced with Co atoms. Therefore with increase in the off time between pulses, the Co-rich, CoZn nanowires were formed. On the basis of these contents the point is; we can control nonmagnetic element content in Co_xZn_{1-x} alloy nanowires by increasing off times in a relatively wide range.

Hysteresis loops of as prepared CoZn alloy nanowires applying external magnetic field parallel to long-axis of the nanowires at room temperature were obtained. The magnetic properties of annealed samples at 580 °C in a mixture of 15% hydrogen and 85% argon gases were also examined. The hysteresis loops of both the as prepared samples and annealed ones synthesized at 10, 50, 400 and 600 ms off times are displayed in Fig. 3. As shown in this figure, coercivity, magnetization, and squareness of the samples increases with increase in the off time between pulses. This trend was not exactly seen for the annealed samples. Magnetization and coercivity show a peak around 50 ms off time for the annealed samples. Coercivity of the as prepared samples with 10 ms off time increased to 1325 Oe from initially 170 Oe after annealing. The squareness of this sample was also increased to 0.66 from 0.36. It was also seen the coercivity and squareness of the samples fabricated at 600 ms off time increased to 1770 Oe and 0.87 after annealing from initially 455 Oe and 0.59 respectively. Although magnetization of samples was increased after annealing, the rate of increasing was reduced with increase in the off time between pulses which is accompanied with increase in the Co content. As evidence, the magnetization of samples prepared with 600 ms off time (CoZn nanowire arrays with highest Co content) was not so much changed after annealing.

The variation of the longitudinal coercivity and magnetization of as prepared and annealed samples as a function of off time were determined with the external field applied along the wire's axis and displayed in Fig. 4. Although coercivity of the samples initially (10–200 ms) shows no significant variation, in the range of 200–600 ms off times it almost becomes more than twice. In the range of 10–200 ms, the relative variation of coercivity for the annealed samples was the same as that of as prepared ones

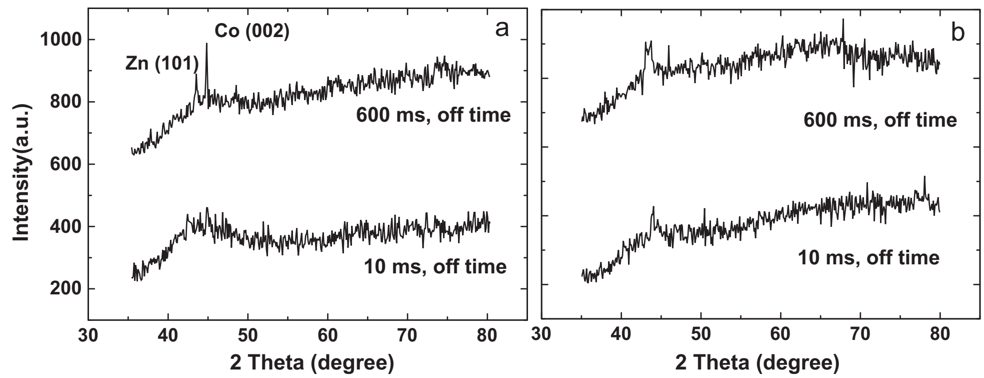

Fig. 5. X-ray diffraction pattern of (a) as prepared and (b) annealed samples fabricated with 10 ms and 600 ms off times.

while coercivity variation of the annealed samples prepared with 200–600 ms off time is less than that of as prepared samples. From 200 to 600 ms off time coercivity variation of annealed samples was nearly 25% while it was more than twice for the prepared samples as mentioned before. An almost 2.6 times increase in the magnetization was observed for the samples prepared with 50 ms off time after annealing while the magnetizations of as prepared samples at 600 ms off time and annealed ones were almost the same. It is anticipated that increasing off time replaces the Zn with Co atoms through electroless procedure forming a mixed phases in which, the size of magnetic grains increases to a critical size and causes an increase in both the coercivity and magnetization. The increase in magnetization of annealed nanowire arrays may caused by the changes of Co particles in the annealing process. It may be said that increase of saturation magnetization is related to the formation of larger Co cluster during the annealing process.

For samples with less Co content, the magnetic atoms were individually distributed between nonmagnetic Zn atoms and could not show their real contribution in the magnetization. Formation of magnetic Co clusters during annealing procedure enhances the saturation magnetization and coercivity of these samples. In samples with higher Co content relatively larger magnetic grains were formed and annealing process has less effect on the magnetic cluster formation and less increase in the magnetization was observed. For theses samples, during annealing procedure, CoZn alloy phase is transferred to solid-Co and liquid-Zn and Co grains with uniform size recrystallize in liquid Zn. It may be said that the resulting Co is polycrystalline and are segregated by the Zn particles. The residual Zn solidified when the samples were cooled down and became pins between Co particles. Higher coercivity might be resulted from nanocrystalline Co grains uniformly distributed in the nanowires and also pinning effect.

To estimate the influence of the off time on the microstructure of the nanowires, X-ray diffraction pattern of as prepared and annealed samples were performed at room temperature. In order to omit the back ground, coming from the aluminum substrate, the aluminum was removed as we mentioned elsewhere [23]. As seen in Fig. 5(a) the samples made at 10 ms off time has an almost amorphous structure as reported by Xu et al. [22]. Small peak observed between 40 and 45° may be an indication of very fine crystal grains of Co and Zn formed in this sample. Increasing the off time to 600 ms increases the crystallinity of the samples thereby intensifies the Zn and Co peaks located around 43.18 and 44.46°, respectively. Although because of more Co content in these samples the peak intensity of (0 0 2) Co is much higher than that of the (1 0 1) Zn. Increase in the degree of crystallinity with increase in off time may be resulted from tranquil electrodeposition during a relatively long deposition time. It may be also said that replacing more Zn with Co in the CoZn alloy nanowires during 600 ms off time forms a crystalline magnetic Co phase. Crystal structure of samples obtained with 10 ms did not change after annealing unless a relatively broad peak was seen for these samples around 44° which may be an indication of very fine crystal formation within amorphous phase (see Fig. 5(b)). X-ray diffraction pattern of the sample fabricated with 600 ms shows a quite different structure after annealing. Although as prepared sample with 600 ms has quite distinct peak, it shows peaks with relatively lower intensity after annealing. A small peak around 51.33 may be an indication of (1 1 1) Co fcc formation in this sample. The treatment of CoZn nanowires may therefore be demonstrated as following. Since the annealing temperature (580 °C) is much higher than melting point of Zn (the melting point of bulk Zn is about 420 °C), as noted above, the Co atoms aggregated during the annealing procedure and formed Co clusters with Zn atoms in the boundaries so that increased both the coercivity and magnetization. This phenomenon is also observable when the off time reduces down below 200 ms. Adding the off time more than 200 ms, increases the Co content of as deposited samples to a relatively high amount so that annealing has no significant effect on the composition variation of CoZn nanowires. On the other hand, although coercivity of high Co content nanowires after annealing was high, their crystal structures were the same as those samples prepared with 10 ms off time.

4. Conclusion

Co_xZn_{1-x} nanowire arrays were fabricated by ac pulse electrodeposition with various off times between pulses changing from 10 to 600 ms.

Our investigation on the effect of off time between pulses on the composition, microstructures and magnetic properties of CoZn nanowire arrays enables us to reach the following conclusions:

It was found that Co content increased by increasing the off time between pulses, using an electrolyte with a constant concentration of Co^{+2} and Zn^{+2}. This phenomenon enables us to fabricate Zn-rich and Co-rich nanowires by adjusting the off time during the deposition procedure. Increasing the off time between pulses more than 200 ms increased the coercivity and squareness of CoZn nanowires arrays.

A significant increase in the coercivity of CoZn nanowires was observed after annealing which was related to the electrodeposition conditions.

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