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CoFe Layers Thickness and Annealing Effect on the Magnetic Behavior of the CoFe/Cu Multilayer Nanowires

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Abstract

CoFe/Cu multilayer nanowires were electrodeposited into anodic aluminum oxide templates prepared by a two-step mild anodization method, using the single-bath technique. Nanowires with 30 nm diameter and the definite lengths were obtained. The effect of CoFe layers thickness and annealing on the magnetic behavior of the multilayer nanowires was investigated. The layers thickness was controlled through the pulses numbers: 200, 260, 310,360 and 410 pulses were used to deposit the CoFe layers, while 300 pulse for the Cu layers. A certain increase in coercivity and squareness of CoFe/Cu multilayer nanowires observed with increasing the CoFe layer thickness and annealing improved the coercivity and decrease squareness of CoFe/Cu multilayer nanowires. First order reversal curves after annealed showed amount domains with soft magnetic phase, it also shows decreasing spreading of distribution function along the H_u axis after annealed.

1. Introduction

Magnetic nanomaterials made by various methods [1]. Among these nanomaterials, nanowires are of intense interest many ways for fabrication of nanowires have been developed [2-3]. Among the various fabricating methods of magnetic nanowires [4, 5, 6], electrodeposition in porous anodic alumina (PAA) membranes is an effective method, through which nanowires with uniform diameters and high aspect ratios can be prepared [7]. Many ferromagnetic nanowires of Fe, Co, Ni and their alloys are made by this method. Howerer, these nanowire often lose their coercivity due to demagnetization by consanguinity magnetic domains. In order to overcome this defect, the nonmagnetic layer (NM) is inserted between each ferromagnetic layer (FM), to form FM/NM/FM/…. Periodic structure. The magnetic properties of these multilayer nanowires can be varied according to the thickness of FM and NM layers [9]. Hysteresis loop as a common way to research the magnetic properties dose not present a perfect picture of the magnetic phases and interacting field distribution. A more precise method to investigate the magnetic properties is the first order reversal curve (FORC) which was presented by mayergoyz et al. [10] and is known as finger print of the magnetic systems [11]. This method enables researching the coercive field and magnetostatic interaction distributions [12-14]. A single curve of FORC diagram consist of the magnetization as a function of applied (H) and reversal (H_r) fields. The FORC distribution is calculated as follows:

$$\rho_{FORC}(H,H_r) = -\frac{1}{2}\frac{\partial^2 M(H,H_r)}{\partial H \partial H_r} \quad (1)$$

and presented in a contour plot form with 2 orthogonal axes; critical field H_c ($H_c = (H - H_r)/2$) and local interaction field H_u ($H_u = (H + H_r)/2$) [10,15]. This way can be used to research the magnetization behavior of a sample as a contribution of single-domain (SD), multi-domain (MD), pseudo-single domain (PSD), super paramagnetic (SP) particles, coercive field distribution and magnetic interactions between the magnetic domain [12-13], also the effect of different parameters such as particle size [14], structure and temperature [16] on the magnetic properties can be precisely studied by FORC diagrams [17]. In this work we report the synthesis of an array of CoFe/Cu multilayer nanowires. The relationship between magnetic properties and layer thickness are discoursed. The effect of annealing on the microstructure and magnetic properties of nanowire were studied.

2. Experimental:

The PAA template have been prepared using the two-step anodization process [10, 11]. Aluminum foils (99.999%) electropolished in a solution of perchloric and acid-ethanol (1:4 volume ratio) at 20 V for 3 min. The foils were then anodized in 0.3 M oxalic acid solution at 40 V direct current (DC) voltage and constant temperature of 17℃ for 5 h. The anodized foils were then dipped in a mixture of 0.2 M chromic and 0.5 M phosphoric acid solution at 60 ℃ or 10 h to remove the anodized layer. The foils were re-anodized as the first step for 3 h. Subsequently, the barrier layer thickness was decreased to 12 nm by a non-equilibrium anodization process [20]. CoFe/Cu multilayer nanowires were electrodeposited with the single-bath way. The electrolyte temperature was kept as 30℃ ; the sample and a graphite rode were used as working and counter electrodes, respectively.

The electrolyte was a solution composed of 0.15 M $FeSO_4.7H_2O$, 0.15 M $CoSO_4.7H_2O$, 0.05 M $CuSO_4.5H_2O$, 1 gr/l ascorbic acid and 45 gr/l boric acid. The acidity of electrolyte was 4. Multilayer nanowires were ac-pulse electrodeposited into the template using reduction/oxidation voltage and off-time of 18/12 V, o ms and 12/12 V, 300 ms, for CoFe and Cu segments, respectively.

Impurity of each one was controlled through the maximum deposition current during the reduction in the constant 3.5 and 32 mA value to deposit the Cu and CoFe segments, respectively. To control the thickness of each layer, the different pulse numbers of 200, 260, 310, 360 and 410 were used to deposit the CoFe layers and 300 pulse number was used to deposit the Cu layers, then samples annealed at 570 ℃ in a mixture of 15% hydrogen and 85% argon gases for 30 min. The morphology and microstructure of the samples were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The chemical composition of the samples was analyzed using X-ray fluorescent (XRF). The layer thickness of the obtained multilayer nanowire was estimated by transmission electron microscopy (TEM). For TEM measurements, the template were etched in 0.3 M NaoH solution and then ultrasonically dispersed in distilled-water before being dropped on a carbon coated copper grid. The magnetic properties consisting hysteresis loops and FORC diagrams were investigated by vibrating sample magnetometer (VSM) at room temperature.

3. Result and Discussion:

Figure 1 shows the typical SEM image of the nanopore arrays prepared after the second anodization. The hexagonal structure with 30 nm diameter and 100 nm pores distance can be seen.

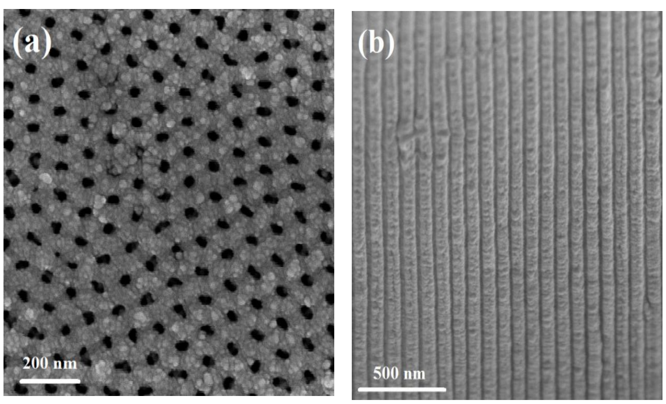


Fig. 1. SEM images obtained from: (a) top-view and (b) cross section of highly ordered PAA template after the second step.

The bright field TEM image of the deposited CoFe/Cu nanowire arrays with 300 Cu and 410 CoFe pulse is shown in Fig.2. The subsequent Cu and CoFe layers are observed in a bright/dark succession. As shown in Fig.2 the thickness of ferromagnetic and non-magnetic segments of sample are 100 nm and 10 nm, respectively. Since difference in atomic number of the Cu and CoFe segments, multilayer structure with light and dark sections is seen in image, respectively.

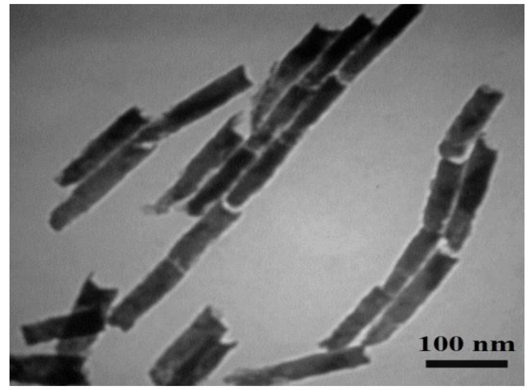
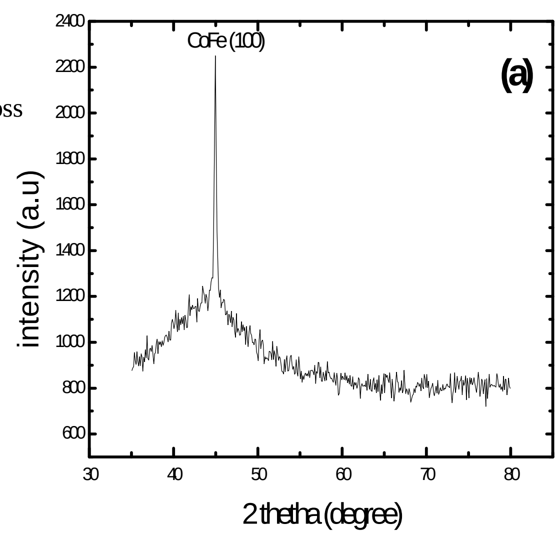


Fig. 2. TEM image of CoFe/Cu multilayer nanowires with 300 Cu pulses and 410 CoFe pulses.

Two samples were fabricated for investigated the Cu and CoFe rate that X-ray diffraction pattern of this samples are shown in Fig.3. The sample 1 fabricated by constant current 3.5 mA and the sample 2 fabricated by 4000 CoFe pulses. In fact sample 1 and sample 2 are seen to be rich of Cu and CoFe, respectively. Fig.3 shows although sample 1 was rich but bcc-CoFe(100) peak at $2\theta = 44.93°$ is seen for sample1.



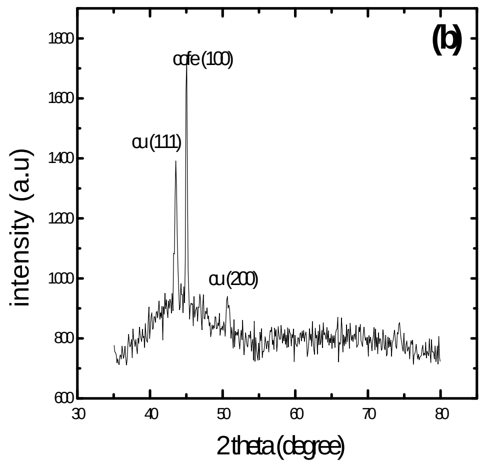


Fig. 3. X-ray diffraction pattern for prepared CoFe/Cu nanowires with (a) 4000 CoFe pulse (b) 3.5 mA constant current for Cu.

The compositional analysis of the electrodeposited CoFeCu alloy nanowires by XRF (see table 1) demonstrated the amount of CoFe impurity in the Cu layer is about 23.42 at.% while that of the Cu impurity in CoFe layer is about 14.15 at.%.

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

Sample	Co (at.-%)	Fe (at.-%)	Cu (at.-%)
CoFe-rich	39.62	46.23	14.15
Cu-rich	10.81	12.61	76.58

Hysteresis loops of the multilayer nanowires were measured by external magnetic field applied parallel to the wires axis (out-of-plane) at room temperature. The hysteresis loops of samples as prepared and annealed at 200 and 360 CoFe pulses and 300 Cu pulses are displayed in Fig.4.

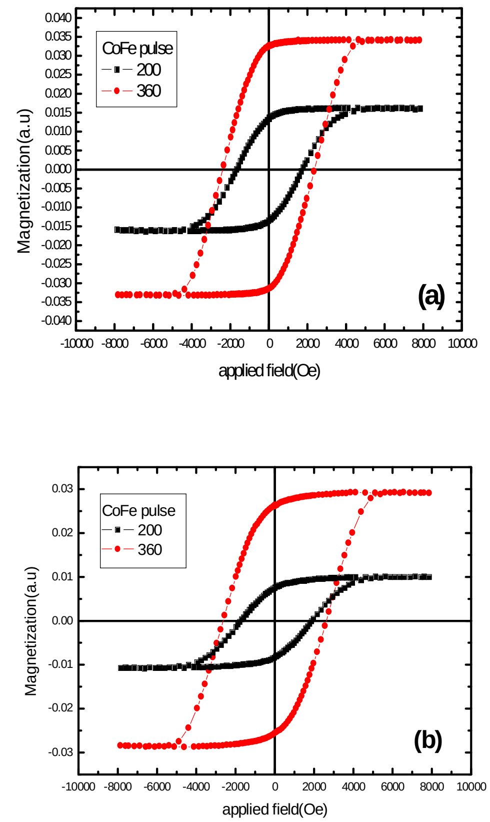


Fig. 4. The hysteresis loops of (a) as-prepared and (b) annealed samples with 300 Cu pulse and 200, 400 CoFe pulse.

The reduction of CoFe pulses, that proportional with reduction of CoFe layer thickness[21], leads to reduce coercivity and squareness $S_q=M_r/M_s$ of the as-prepared and annealed samples until for 360 CoFe pulses this amount to are become maximum and then with the reduction of CoFe pulses coercivity and squareness decreases(see Fig.5). As shown with increasing of CoFe pulses from 200 to 360 and also with annealed coercivity increases because the increase of CoFe layer thickness leads to increase the wire length thereby increases the shape anisotropy of the wire and then the coercivity of samples increase . When the CoFe pulses increase to 410 the coercivity decreases because interaction reduces.

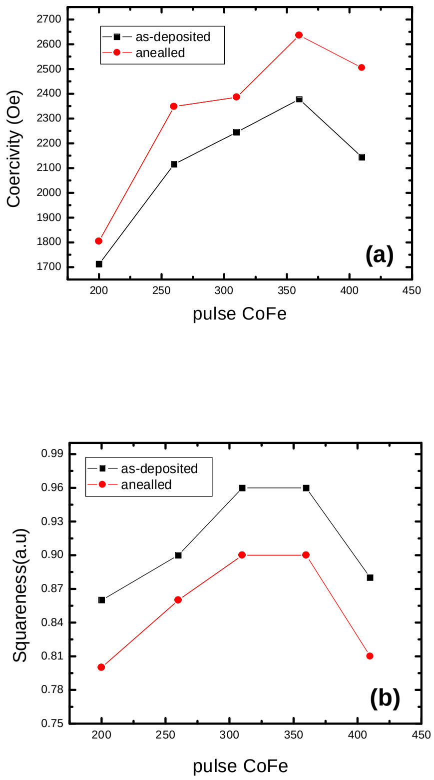


Fig. 5. (a) coercivity (H_c) and (b) The squareness (S_q) of prepared and annealed samples as a function of CoFe pulses.

It is obvious that squareness decreases after annealed while expected to the increase coercivity after annealed leads to increase the squareness. Following FORC diagrams were employed for investigation the decrease of annealed samples squareness.

FORC diagrams were measured in OOP state at room temperature. To plot this diagram the maximum applied field was 6000 Oe with 200 Oe intervals and smoothing factor was 2. FORC diagram for as prepared sample is demonstrated spreading of distribution function along the H_u axis (Fig.6). After annealing spreading of distribution function along the H_c axis increases. As shown domains are exist with different coercivity and coercivity of samples is the average coerciviy of all domains. Increasing spreading of diagram along the H_c axis after annealing shows coercivity of nanowire increases [17, 22]. A relatively weak soft phase is observed around the H_c =0 in Fig.7, therefore it may be said squareness after annealing decrease because soft phase is exist and so the interaction decrease. With more investigation in Fig.7 it can be seen center of diagram about 400 Oe is rise of H_c axis and the segment of diagram that is parallel with H_u axis was curved in comparison to axis parallel with H_u axis. Therefore the demagnetizing interaction is overcome on the demagnetizing interaction [23] so interaction for this sample is demagnetized.

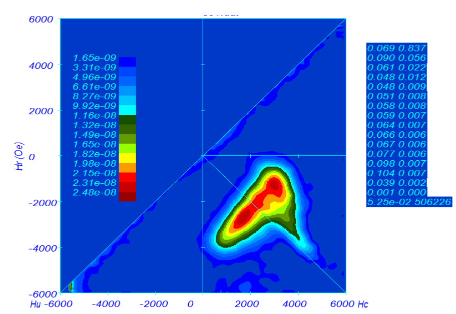


Fig. 6. FORC diagram of prepared sample fabricated with 300 Cu pulse and 360 CoFe pulse.

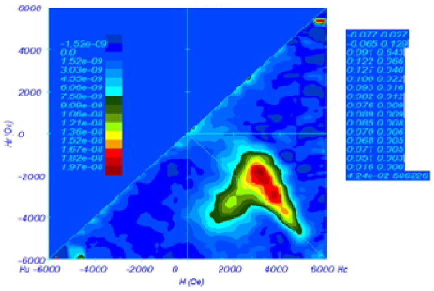
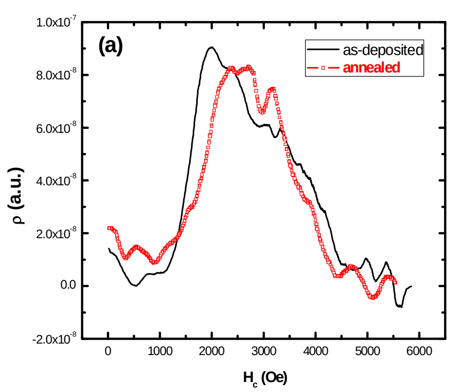


Fig. 7. FORC diagram of annealed sample fabricated with 300 Cu pulse and 360 CoFe pulse.

The cross sectional view of FORC distribution along the H_c and H_u axises are presented in Fig.8. As can be seen annealing increases amount of domains with more coercivity and curve shows two peak that the peak intensity of the first peak (that has more coercivity) is higher. It is justify existence one single domain with high coercivity and amount domains with fewer coercivity after annealed. Both the peaks have coercivity more than the peak of sample before annealed, as a result coercivity increase with annealed.

The cross sectional view of FORC diagram along the H_u axis (Fig.8) shows the intensity of peak decrease with annealed, also decrease interaction so we conclude after annealed squareness decrease because the interaction decrease.



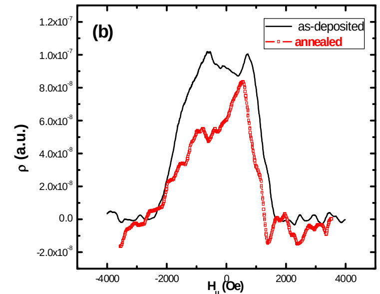


Fig. 8. cross section FORC distribution along (a) the H_c axis (b) the H_u axis of CoFe/Cu multilayer nanowires synthesized with 300 Cu pulse and 360 CoFe pulse.

To investigate the effect of non-magnetic layer thickness on the interaction two samples were fabricated with 360 CoFe pulse and 200 and 400 Cu pulse. As shown in Fig.9 after this CoFe pulse increase to 360 , the change of cu layer thickness dose not influence on the magnetic properties CoFe/Cu multilayer nanowires, hence the optimum Cu pulse for samples was fabricated with maximum CoFe pulse is 300.

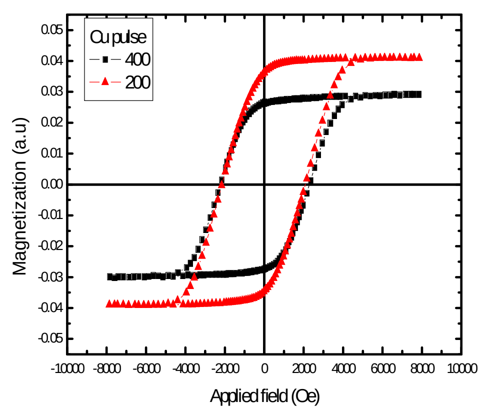


Fig. 9. The hysteresis loops of as-prepared samples with 360 CoFe pulse and 200, 400 Cu pulse.

To investigate the effect of annealing on the microstructure of nanowires, the X-ray diffraction pattern of samples as-prepared and annealed were performed at room temperature. In order to remove the background, coming from the aluminum substrate, the alumina was removed as we mentioned elsewhere [24]. As seen in Fig.9 the nanowires are polycrystalline since almost all the permitted reflection are observed. As can be seen from Fig.10 (a) and (b), annealing does not change crystalline phase and bcc-CoFe(110) peak at 2θ= 44.93° observed for two X-ray diffraction patterns. It seen that intensity of the CoFe peak increases a few after annealed about 13%.

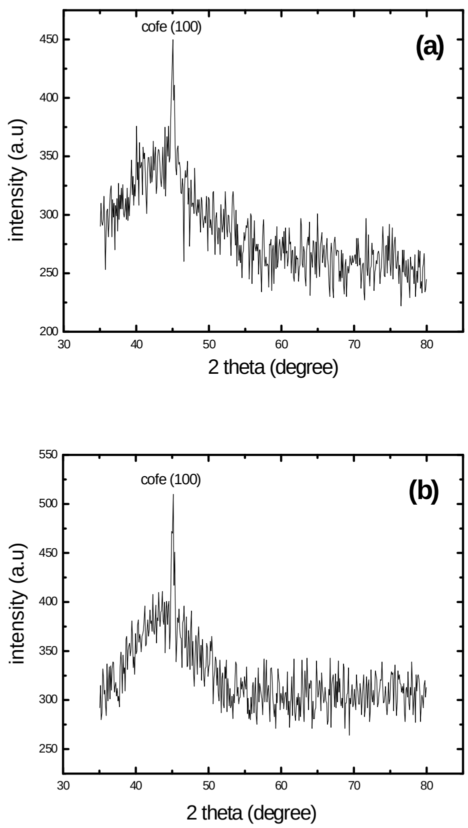


Fig. 10. XRD patterns of samples with 300 Cu pulse and 360 CoFe pulse (a) as prepared (b) annealed.

4. Conclusion:

The CoFe/Cu multilayer nanowires were prepared using the single-bath method. With difficult thickness of the magnetic layers and annealing, the following results were obtained:

1) With increasing the pulse number of CoFe layer from 200 to 410, the coercivity increases to optimum values of 2378 Oe then decreases.

2) With annealing, the coercivity increase but microstructure of nanowires has change a few.

3) With FORC analysis can be seen squreness of samples decreases after annealed because spreading of distribution function along the H_c axis decreases and to be exist soft phase.

4) After the optimum values for CoFe pulse, changing of thickness of the non-magnetic layer dose not improved magnetic properties of the CoFe/Cu multilayer nanowires.

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