Fabrication of Iron Nanowire Arrays Using Nanoporous Anodic Alumina Template

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In this work, electropolishing combined with a two-step anodization process at moderate anodization voltages of 140 V in 0.3 M oxalic acid lead to a uniform hexagonally ordered nanoporous structures. A step-down process was used that reduced the insulating barrier layer thickness through which uniform electrodeposition could be achieved. It was demonstrated that using AC electrodeposition and the step-down process leads to uniform iron nanowire arrays. We have employed a template-assisted approach to the fabrication of arrays of iron nanowires with the possibility to design the height and diameter of the iron nanowires only by varying the parameters of the preparations conditions. The surface roughness is associated with the fluctuations in the growth rate, which is caused by fluctuations in the thickness of barrier layer. According to the SEM images, arrays of iron nanowires have ranging from 1 to 6 µm in length and 66 nm in diameter.

Key Words: Nanowire, Anodization, Nanoporous alumina, Electrodeposition.

INTRODUCTION

Magnetic nanowires are scientifically interesting and have potential applications in the wide ranges of advanced nano-technology, including patterned magnetic recording media[1,2], materials for optical and microwave applications[3,4], electro-luminescent display devices[5] and biological applications[6,7]. Magnetic nanowire arrays can be fabricated by electrodeposition in nanoporous templates. Highly ordered templates of pre-determined channel length, diameter, width and density are required. By depositing metals into the nanopores, nanowires with a diameter predetermined by the diameter of the nanopores are fabricated. If one dissolves away the host solid material, free-standing nanowires are obtained. It is well known that anodization of aluminum in acidic solutions leads to a nanoporous alumina template. A two-step anodization process leads to a hexagonally ordered nanoporous alumina template in which the range of order extends to areas of the order of µm^2. Thus by controlling the anodization voltage the pore size and distribution of the pores can be easily tailored. Electrodeposition is an economical and versatile method for fabrication of magnetic nanowires. Conventional technologies used to obtain nanostructures, such as e-beam lithography, X-ray lithography and scanning probe based lithography are relatively expensive and not always suitable for commercial applications. A distinct advantage of the simple electrodeposition process is the ease of alloy deposition and the availability of various process parameters like electrolyte composition, bath pH and mode of deposition (DC, pulse and AC) that can be varied easily to get the desired material properties. There have been various reports in the literature where nanowires have been made of Fe, Co, Ni metals and their various binary alloy combinations[8-12].

EXPERIMENTAL

Nanoporous alumina films are obtained by electrochemical oxidation of high-purity (> 99.998 %) aluminum foils. Prior to anodization, several cleaning treatments are employed. The sample is first degreased in ethanol, followed by soft chemical polishing in acetone and inside the ultrasonic bath for 7 min, which removes the native oxide layer, being then rinsed in deionized water. In the work here presented, in the first step, the anodizatin voltage is 40 V voltages during 10 min and then a hard anodization procedure is used in order to achieve the desired organization of pore structure. The hard anodizations were performed at constant 140 V during 1 h. As electrolyte 0.3 M oxalic acid solution was used and the temperature was kept constant within 0 ºC. The thinning of barrier layer can form a routed structure at the bottom side of the anodic alumina nanopores and the subsequent electrodeposited

iron nanowire. For this reason, barrier layer modification accomplished at the end of secondary anodizing process to thinning thick barrier layers to adjust its thickness to approximately 30 Å. For electrodeposition process, we have used an electrolytic solution of 8.34 g/L $FeSO_4.7H_2O$, 4.5 g/L boric acid and 0.1 g/L ascorbic acid. Electrodeposition on the barrier layer requires high negative polarization in order to overcome its resistance. A thinner barrier layer results in a considerable decrease in the potential barrier for the electrons to tunnel through the barrier layer during electrodeposition at the bottom of the pores. After thinning the barrier layer, a systematic series of experiments of AC electrodeposition of iron nanowires into porous alumina were conducted by varying the AC voltage within the range of -15 until 15 V with a constant frequency of 200 Hz at 24 ºC. Embedded iron nanowires were examined by SEM to determine the degree of pore-filling. Prior to SEM investigations, the unfilled matrix of porous alumina above the filled fraction was partially stripped in a solution of 100 mL NaOH for 10 min. Unfilled alumina was selectively dissolved in the solution while the iron nanowires were stable under these conditions.

RESULTS AND DISCUSSION

Fig. 1. gives the current-time, charge-time and voltage-time curves for aluminum anodization in 0.3 M oxalic acid. In the beginning, the current is high due to the fact that the current only passes through the metallic aluminum. Then the current starts to decrease because of the formation of a thin non-porous oxide layer. This oxide layer has a higher resistance than the metallic aluminum. The increase in thickness and therefore an increasing resistance result in a further decrease in the current. The barrier layer modification has a fundamental rule in the uniformity of electrodeposited iron nanowire arrays. Anodic alumina template with thick barrier layers must be modified so that the electrons can pass the barrier layer by tunneling. On the other hand, the thin barrier layers must be thickened to gain appropriate mechanical strength to tolerate the heat of anodized process. Moreover, another important factor for the quality and the homogeneity of the embedded iron nanowires is the thickness of the insulating barrier oxide layer. On the other hand, electroactive iron ions electromigrating into the nanochannels have to be supplied to the barrier
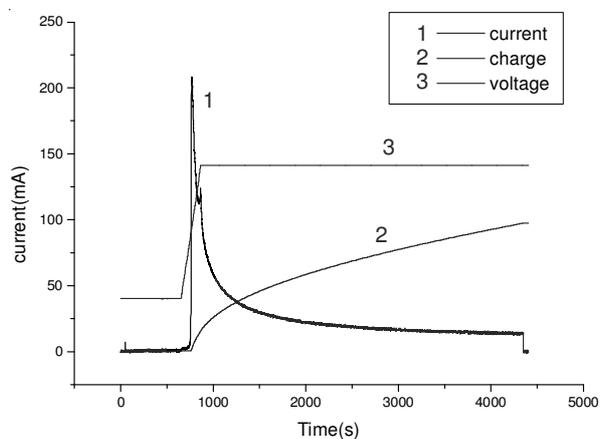
layer fast enough in order to achieve homogeneous electrodeposition. Therefore, the concentration of iron ions has to be as high as possible otherwise hydrogen evolution can become predominant.

The quality and distribution of the iron nanowires in the anodic alumina template was examined by SEM (Fig. 2). Nano-scale templates play an important role in forming iron nanowires.
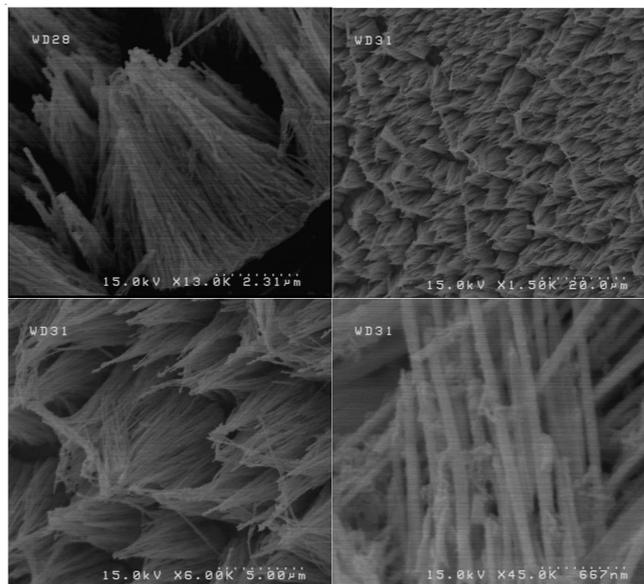

Fig. 2.   SEM image of liberated iron nanowires after the alumina matrix is selectively dissolved in a solution of 100 mL NaOH for 10 min

AC electrodeposition of iron with a frequency of 200 Hz enabled us to achieve relatively high current densities. It is known that the depletion of iron ions along each pore and their transport depend on the applied AC frequency and hence affects the homogeneity and the degree of pore filling. At the beginning of the AC electrodeposition, after 10 second, a sudden increase of the current density was observed, at which time the first pores were overfilled, then, the current density started at 0.05 A cm^{-2} and afterward decreased to 0.01A cm^{-2}. Iron nanowires exhibit a distribution with a mean diameter of 66 nm. Although some of the nanowires are still embedded into the matrix and their lengths cannot be measured directly, it can be seen that some of them exceed 6 μm in length. This proves that the method can be successfully applied to fabricate high-aspect ratio iron nanowires.

Conclusion

The fabrication of nanopores anodic alumina template from (99.998 %) aluminum foil has been successfully demonstrated using two step anodization process. The structure and morphology of anodic films were greatly influenced by the voltage type and anodization duration. In the modified two-step anodization process, the best result was obtained with using 40 V anodization voltage for the first anodization step and then increase to 140 V for the second anodization step. It is concluded that an applied potential of 140 V gives the best conditions for the appearance of organized patterns (Fig. 2). Iron nanowires were prepared by AC pulse electrodeposition with controlled pulse schedule using a homogeneous hexa-

Fig. 1.   Current-time curves for anodization process by 0.3 M oxalic acids and 140 V anodized voltage

gonally arrayed anodic alumina matrix as the template. According to Fig. 2, iron nanowires exhibit a distribution with a mean diameter of 66 nm.

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