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Pulsed electrodeposition of monocrystalline Ni nanowire array and its magnetic properties

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ABSTRACT

By means of a porous template without removing the aluminium substrate, a technique of pulsed electrodeposition with an intermittent symmetric square pulse has successfully been applied to fabricate Ni nanowire array. The as-obtained nanowires have a diameter of about 60 nm and exhibit high aspect ratio of more than 50. The electron diffraction pattern investigation demonstrates that the nanowires are single crystal. Moreover, a highly preferential orientation [2 2 0] of the as-obtained Ni nanowires with high purity decided by XRD has been obtained, and the preferred orientation is weakened remarkably by an annealing process. Furthermore, the investigation of magnetic properties by VSM indicates that the as-obtained Ni nanowire array has an obvious magnetic anisotropy and exhibits a good thermal stability.

1. Introduction

In recent years, the synthesis of one-dimensional nanostructures has attracted great interest because of their contribution to the understanding of basic concepts and potential applications [1–3]. Among the different approaches to the fabrication of nanowires, the alumina template-based synthetic methods have received considerable attention due to its several unique structure properties, such as controllable pore diameter, extremely narrow size distribution for pore diameters, and ideally cylindrical shape of pores. Especially, the template electrodeposition has been proved to be effective way to fabricate metal and its alloy nanowires [4,5].

According to the applied electronic waves, the template electrodeposition can be divided into two types, i.e. direct current (DC) [6] and pulsed electrodeposition [7–9]. The pulsed electrodeposition usually contains an alternating electrodeposition (AC) and the pulsed electrodeposition with square and other complex electronic pulses. In present paper, the latter is specified as PED. Prior to DC electrodeposition, the aluminium substrate and the insulated barrier layer between the aluminium substrate and the porous layer at the outer part of the alumina film have to be removed. At the same time, a conductive layer of metals has to be deposited on the one side of the continuous holes film, serving as the cathode during the DC electrodeposition. Therefore, the procedure for DC deposition is relatively complex. Furthermore, the metal introduced is usually Au or Pt, which is very difficult to be removed due to its inactive chemical property in the subsequent investigation of the obtained sample. In contrast to DC deposition, since the AC deposition makes use of the rectification character of the barrier layer to carry out deposition, the aluminium substrate and barrier layer during the process of AC deposition cannot be removed, therefore, the procedure for AC deposition is simple, and the aluminium substrate can be easily dissolved by a chemical etching process. However, the filling fraction of nanoholes for the AC deposition is generally lower due to the high potential applied that causes oxygen or hydrogen evolution on the surface of alumina template so as to inhibit the deposition.

The PED is generally regarded as a reliable way for growth of uniform and continuous nanowires in the alumina template due to its better ability of electroplating materials in deep holes. Pretreatment of the alumina template before PED has two different methods. The first method is similar to that of DC electrodeposition mentioned above, therefore, the disadvantages for DC electrodeposition also exist in such PED. However, like AC electrodeposition, the second method need not dissolve the aluminium substrate and barrier layer. The nanowires are straightforwardly electrodeposited on the tips of nanoholes and the procedure is really simple. Also, the previous investigations [10,11] have

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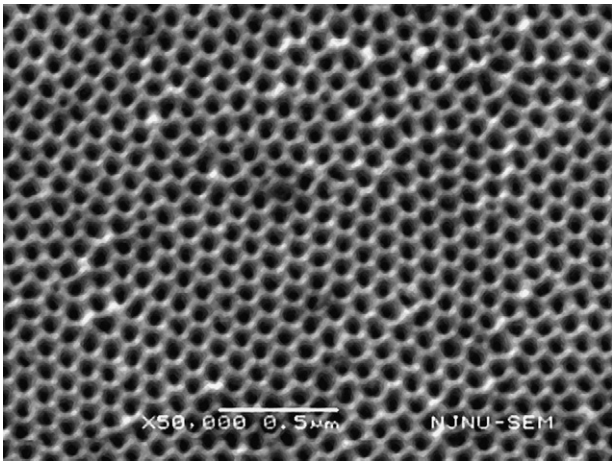

Fig. 1. SEM micrograph of the as-obtained alumina template by a two-step anodization.

indicated that nearly 100% filling of nanoholes can be achieved by PED with a modulated pulsed wave. Therefore, it is great interesting for us to fabricate nanowires by the second PED.

In this paper, we report the pulsed fabrication of monocrystalline Ni nanowire array by the second PED with an intermittent symmetric square. The as-obtained nanowire array has been observed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometer (XRD), the selected area electron diffraction (SAED) and vibrating sample magnetometer (VSM). At the same time, the effect of an annealing process on the structure and magnetic properties of the as-obtained array has been investigated.

2. Experimental details

Al foils (purity 99.999%, thickness 3 mm) were anodically oxidized in an oxalic acid solution at 0 °C and 40 V to prepare the alumina template by a two-step anodization method, as described in ref. [12]. The obtained template has been indicated in Fig. 1. The duration of the second step anodization is 1 h, and the length of the as-obtained nanopores in the alumina template is about 15 μm. After the second step anodization, a technique of reducing the voltage to 5–6 V in a series of small steps, was applied to thin the barrier layer to better the subsequent electrodeposition. Especially a long duration at 5–6 V was to be maintained to uniform the thickness of the barrier layer in order to keep the deposition homogeneous throughout the alumina template. Then Ni nanowires were electrodeposited in the nanoholes of alumina template by PED with an intermittent symmetric square pulse. The fabrication of Ni nanowire array was carried out using the process shown schematically in Fig. 2.

The pulsed electronic signal was supplied by a Partstat 2273 Advanced Potentiostat/Galvanostat/FRA system under a current controlled mode (see Fig. 3). A Pt and Ag/AgCl electrodes were

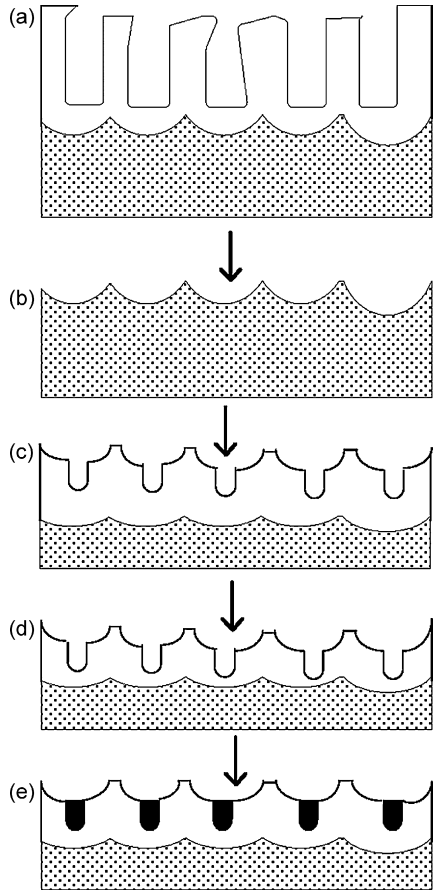

Fig. 2. Schematic diagram for fabrication of monocrystalline Ni nanowire array by the PED: (a) porous alumina film after first anodizing; (b) pre-structured aluminium substrate by removing the porous alumina layer; (c) highly ordered porous alumina template obtained by a second anodization step; (d) highly ordered porous alumina template with a thinned barrier layer; (e) Ni nanowire array fabricated by the PED.

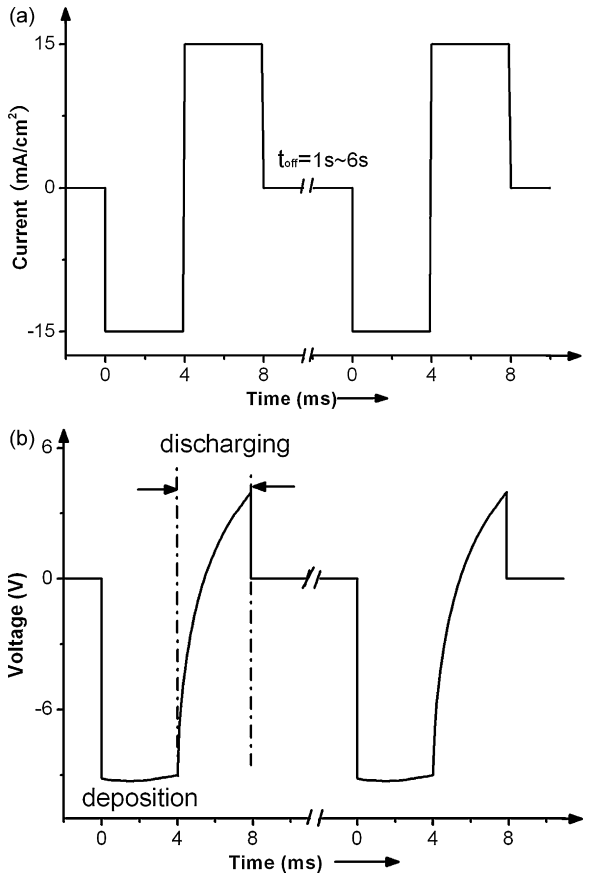

Fig. 3. Current-time (a) and voltage-time (b) curves for PED. First, a current-limited negative pulse is applied to deposit Ni. Then a positive pulse is applied to discharge the capacitance of the alumina barrier layer. The cycle is repeated after t_{off} (1–6 s) in order to avoid depletion of metal ions near the deposition interface.