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Fabrication and magnetic properties of Ni–Zn nanowire arrays

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ABSTRACT

Ni–Zn nanowire arrays, with diameters of approximately 60 nm and lengths of around 40 μm, were fabricated by electrodeposition in porous anodic aluminum oxide templates at different electric potentials. X-ray diffraction observations demonstrated that the isolated nanowires had polycrystalline structure and that their phases changed with the deposition potential. The amount of deposited zinc in the nanowires increased with the deposition potential, whereas the amount of nickel decreased. Magnetic measurements showed that there was a gradual change of magnetism from isotropic to anistropic with increasing potential amplitude and that the coercivity reached a maximum value in the nanowire deposited at −1.35 V.

1. Introduction

Recently, one-dimensional and quasi-one-dimensional nanostructured materials have attracted considerable interest because of their applications in optics and high-density perpendicular magnetic recording media and much effort has been expended on the synthesis of these materials [1–4]. Among the different preparation procedures, the most widely used is the template method [5–7]. Compared with other templates [8,9], the anodic aluminum oxide (AAO) template is ideal for preparing ordered nanotube arrays using electrochemical methods because of its uniform and nearly parallel porous structures.

In this paper, we investigate the preparation of an array of highly ordered Ni–Zn nanowires by DC electrodeposition into porous AAO templates [8,10]. The structure of the nanowires has been investigated using conventional X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), while the magnetic properties have been measured using a vibrating sample magnetometer (VSM).

2. Experimental procedure

Porous anodic aluminum oxide templates were prepared using a two-step anodizing process [11]. Aluminum foils 0.28 mm thick and with purities of 99.999% were anodized for 10 h in 0.3 M oxalic acid solution under a constant potential of 40 V at 10 °C. Following anodization, the remaining aluminum was removed using a saturated $CuCl_2$ solution. Etching treatment was then carried out in 6 wt% H_3PO_4 at room temperature for 2 h to remove the barrier layer on the bottom side of the AAO and obtain a template with holes passing through the entire thickness of the foil. This process resulted in AAO templates with a pore length of about 40 μm and a nearly uniform diameter of about 60 nm. Afterwards, a 300 nm Cu layer was sputter-deposited onto one side of the AAO, this served as the working electrode for the following electrodeposition.

The pH of an aqueous bath containing 0.1 M $NiCl_2 \cdot 6H_2O$, 0.1 M $ZnCl_2$ and 0.01 M glycin was adjusted to 2.5 by adding appropriate amounts of dilute HCl. Electrodeposition was carried out at a constant potential of −0.9 to −1.46 V in a conventional geometry consisting of a graphite rod counter electrode and an Ag/AgCl reference electrode. The porous alumina membranes, with pore diameters of 60 nm and thickness 40 μm, were used as the working electrode. All measurements were carried out at room temperature.

Depending on the deposition potential used, the electrodeposition process lasted 60–120 min. After electrodeposition, a piece of the AAO template now containing Ni–Zn nanowires was dissolved using 5 wt% NaOH, and washed 3–5 times alternatingly with distilled water and ethanol. Afterwards, the nanowires were detached from the substrate by ultrasonic dispersion in 2–3 ml ethanol. A drop of the solution was then placed on a Cu grid with a carbon film and air dried prior to electron microscope analysis.

3. Results and discussion

Fig. 1(a) shows an AFM surface view of an alumina film prepared by the two-step anodization described above. From the

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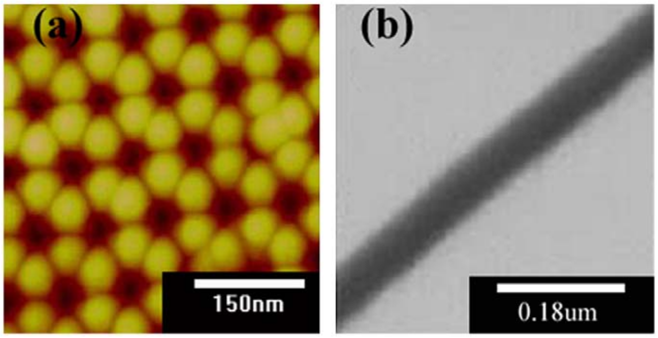

Fig. 1. (a) SPM image of the AAO template with hole diameter of about 60 nm and (b) TEM image of isolated Ni–Zn nanowire liberating from the alumina template.

image we can see that the pores have almost identical diameters of 60 nm and spacings of about 35 nm. The highly ordered white spots correspond to the pores in the AAO template. This special structure of the alumina film makes it promising as a template for fabricating an ordered nanowire array over a large area. Fig. 1(b) is a TEM image of an isolated NiZn nanowire after removing the alumina prepared by electrodeposition for 80 min. The diameter of the nanowires is about 60 nm, which corresponds to the pore diameter in the AAO template shown in Fig. 1(a).

Fig. 2 shows the XRD pattern of aligned NiZn nanowire arrays prepared at different deposition potentials in the AAO templates. For XRD measurements, the Al and AAO substrates were etched away by an amalgamation process using saturated $CuCl_2$ and NaOH aqueous solutions and finally washed thoroughly with distilled water. From the pattern we can see that the Ni–Zn nanowire arrays show different phase structures with different deposition potentials. At low potential, where we adjust the deposition potential to -0.9 V, there is only the face-center-cubic (fcc) Ni phase with the (1 1 1) pattern evident (Fig. 2(a)). However, a peak (1 0 1) of the hexagonal-closed-packed (hcp) Zn phase appears with increasing deposition potential. For the sample prepared at -1.35 V, another interesting feature can be seen. There is a broadening of the peak near $2\theta = 43^\circ$, which may be due to the appearance of a NiZn alloy phase (JCPDS card, 065-3203). When the potential rises to -1.46 V, there are only six diffraction peaks in the XRD pattern, corresponding to the (0 0 2), (1 0 0), (1 0 1), (1 0 2), (1 0 3) and (1 1 0) peaks of hcp Zn. No more extra peaks such as those due to the NiZn alloy or elemental Ni were detected. This indicates that the amount of deposited zinc in the nanowires increases with the deposition potential, whereas the amount of nickel decreases. Consequently, we can conclude that the texture configuration of binary alloy nanowire arrays can be adjusted by changing the deposition potential. From Fig. 2(e) we observe that the intensity of the Zn hcp (1 0 1) peak is the largest, indicating that for Zn nanowires deposited in porous AAO membranes, growth is preferentially along the Zn hcp (1 0 1) direction [12].

In order to investigate more clearly the influence of the doping conditions, magnetic characterization measurements of the hysteresis loops in configurations with the magnetic field parallel($\parallel$) and perpendicular($\perp$) to the NiZn long axis nanowires were carried out. Measurements performed on the AAO templates containing the nanowire arrays were made at room temperature using a Lake Shore 7310 vibrating sample magnetometer in applied magnetic fields ranging up to 5 kOe. The properties of the nanowires are expected to be dependent on the diameter of the nanowires. In our experiments, in order to eliminate the effects of the diameter, all nanowires were fabricated with the same diameter by adjusting the pore size of AAO template [13].

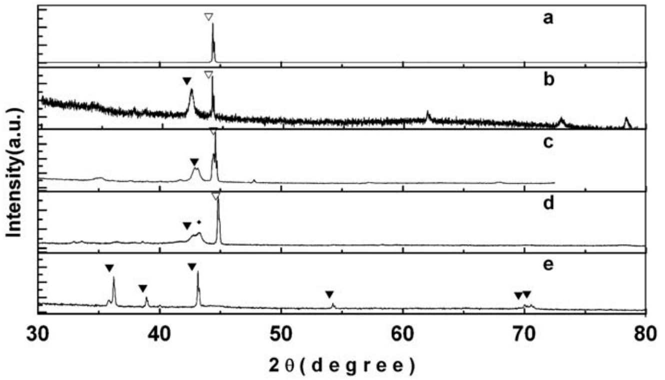

Fig. 2. XRD patterns of aligned Ni–Zn nanowires in the AAO template prepared at different potentials:(a) -0.9 V; (b) -1.12 V; (c) -1.24 V; (d) -1.35 V and (e) -1.46 V. (▽) denotes the peak for Ni; (▼) denotes the peak for Zn and (●) denotes the peak for NiZn alloy.

Typical room-temperature hysteresis loops (M–H) of NiZn nanowire arrays deposited under different electric potentials are shown in Fig. 3((a)–(e)). The saturation magnetization is underlined in each figure. We designate the corresponding magnetic fields as $H_{\parallel}$ and $H_{\perp}$. For the nanowires deposited at -0.9 V, M–H loops in the parallel and perpendicular geometries are almost the same, and there is no apparent magnetic anisotropy (Fig. 3(a)). At low potential, the current between the electrode and electrolyte is low and correspondingly, the whole nanowire is homogeneous. On the other hand, only nickel can be detected in the sample according to the XRD results mentioned above. As a result, we can conclude that the effective anisotropy of the magnetic nanowires results from shape anisotropy, and the magnetocrystalline anisotropy of the nanowires gives only a small contribution in this case [14]. For wire arrays prepared at higher potential, a different behavior can be observed (Fig. 3(b)–(e)). Thus, nanowire arrays show apparent magnetic anisotropy with the increasing potential, which may be due to structural changes caused by the increased concentration of zinc in the nanowires [15]. In particular, the deposition of cations into the alumina template will accelerate with increasing deposition potential [16], and many dispersed structures will form in the wires at high deposition potential. Consequently, intrinsic stress and defects are high in the Ni–Zn nanowire arrays, which leads to an increase in magnetocrystalline anisotropy. In this regard, we suggest that the changes in the magnetic properties are related to structural changes under different deposition potentials.

Table 1 shows the magnetic parameters of nanowires synthesized under different deposition potentials. We can see that the squareness SQ ($SQ = M_r/M_s$ where M_r denotes remanence and M_s the saturation magnetization) of parallel hysteresis loops decreases from 0.55 to 0.23. On the other hand, a distinct change is found in the SQ of the hysteresis loops measured in a perpendicular field. With increasing deposition potential, Zn will be deposited preferentially. The growth process and texture of Ni will then be influenced by tiny regions of hcp-phase Zn, where the magnetocrystalline anisotropy makes a contribution which favors magnetization parallel to the nanowire arrays. Under these conditions the uniformity of nanowires will be destroyed, and we can see that $SQ_{\perp}$ decrease more rapidly than does $SQ_{\parallel}$.

Fig. 4 shows the variation in saturation magnetization and coercivity of Ni–Zn nanowire arrays as a function of the deposition potential. The external magnetic field was parallel and perpendicular to the long axes of the Ni–Zn nanowire arrays as indicated. The values of $H_{c\parallel}$ and $H_{c\perp}$ show different variations as functions of the deposition potential. When the external field is parallel to the long axis of the nanowire, the coercivity first