ELECTRODEPOSITION OF NICKEL NANOWIRE ARRAYS

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Abstract

The synthesis, characterization and assembly of one-dimensional nickel nanowires prepared by template-directed electrodeposition are discussed in this paper. Parallel arrays of high aspect ratio nickel nanowires were electrodeposited using electrolytes with different cations and pH. The nanowires were characterized using X-ray diffractometry and scanning electron microscopy. It was found that the orientations of the electrodeposited Ni nanowires were governed by deposition current densities and electrolyte conditions. Free standing nickel nanowires were subsequently obtained by dissolving the template. Due to the magnetic nature of the nanowires, magnetic alignment was employed to assemble and position the free standing nanowires in the device structure.

Abstrak

Sintesis, pencirian dan susunan bagi nanowayar nikel satu-dimensi yang difabrikasi melalui kaedah elektropemendapan terarah templat dibincangkan dalam kertas kerja ini. Susuntertib selari nanowayar nikel dengan nisbah aspek yang tinggi telah dihasilkan melalui proses elektropemendapan menggunakan elektrolit dengan kation dan pH yang berbeza. Pencirian nanowayar dilakukan dengan menggunakan mesin pembelauan sinar-X dan mikroskop imbasan elektron. Didapati bahawa orientasi nanowayar nikel yang terhasil dipengaruhi oleh ketumpatan arus pemendapan dan keadaan elektrolit yang digunakan. Nanowayar nikel kemudian dibebaskan daripada templat dengan melarutkan templat. Disebabkan sifat magnet semulajadi nanowayar yang terhasil, pelarasan magnet digunakan untuk menyusun dan mengatur kedudukan nanowayar dalam struktur peranti.

Keywords/Kata kunci: nickel, nanowires, electrodeposition, electrolyte

INTRODUCTION

Nanostructure is an intermediate form of matter which exhibits unique mechanical, electronic, optical, mechanic, and chemical properties different from those observed in bulk materials. One-dimensional (1-D) nanostructures such as nanowires, nanotubes, nanobelts and nanosprings have been identified as important candidate materials in future electronic, optical and nanoelectromechanical devices. Metallic nanowires have also been employed as sensors, catalysts, superconductor, nanopipette probes and reinforcing fibers in high-strength/light weight composite materials (Rahman et al., 2004; Xue, Cao and Zhu, 2006; Pirota et al., 2004).

Nickel is an interesting material due to its useful electronic, magnetic and catalytic properties. It is used as electrode material in battery systems as well as gas sensing materials for NO_2 (Neubecker et al., 1997), NH_3 (Hotovy´ et al., 2000) and H_2 (Matsumiya et al., 2002). Various methods have been employed to synthesis 1-D nickel nanowires, such as laser ablation, chemical vapor deposition (CVD), hydrothermal and template-directed electrodeposition.

It has been reported that the ordered pore arrangement in an anodic aluminum oxide (AAO) membrane is well suited as the template for electrodeposition of nanowires because it possesses many desirable characteristics such as tunable pore dimensions, good mechanical properties and good thermal stability (Masuda and Fukuda, 1995). The template-directed electrodeposition has also been proven to be a cheap and high-yield technique to produce large arrays of metal nanowires (Sun et al., 2005; Rabin et al., 2003). In this study, a simple template directed electrochemical deposition technique was employed to synthesize nickel nanowires using electrolytes with different cations and pH and their effects on the crystal structure and morphology of the nickel nanowires were examined using X-ray diffractometer (XRD) and scanning electron microscope (SEM).

EXPERIMENTAL

Nickel nanowires of approximately 200 nm diameters were fabricated by template-directed electrodeposition using commercially available anodized alumina template (Anodisc® from Whatman Inc.) and their typical microstructures are shown in Figure 1. For electrodeposition of nickel nanowires, a Au thin film was first sputtered using Emitech 550 table-top sputter coater on one side of the template through seven consecutive sputtering runs, each at 20 mA for 3 minutes, to serve as the conductive seed layer.

The nickel nanowires were deposited galvanostatically with template serving as the cathode and platinum plate as the anode using GAMRY potentio/galvanostat software. The electrolytes used for the depositions were 1 M $NiCl_2.6H_2O$ and 1 M $NiSO_4.6H_2O$ respectively, with 0.5 M H_3BO_3 as the stabilizer. pH for the electrolytes were adjusted to 1, 2 and 3 respectively by adding HCl or NaOH. Electrodeposition was performed using current densities of 1 mA cm^{-2}, 10 mA cm^{-2} and 50 mA cm^{-2} respectively based on the 1 cm^2 area of the cathode. All of the experiments were conducted at room temperature.

After electrodeposition, the seed layer was removed using gold etching solution constituted of 2.5 g KI, 10 ml I_2 and 90 ml H_2O and the nanowires were released by dissolving the template in 5 M NaOH solution. The nanowires were subsequently concentrated by centrifuging and rinsing in nanopure water to remove the NaOH solution. The suspended nanowires were stored in isopropyl alcohol.

The microstructures and morphology of the nanowires were examined using X-Ray diffractiometer (Panalytical X-Pert PRO MPD) operating at 40 kV and 20 mA using Cu Kα radiation and scanning electron microscope (FEI QUANTA 400) at accelerating voltage of 30 kV.

(a) (b)

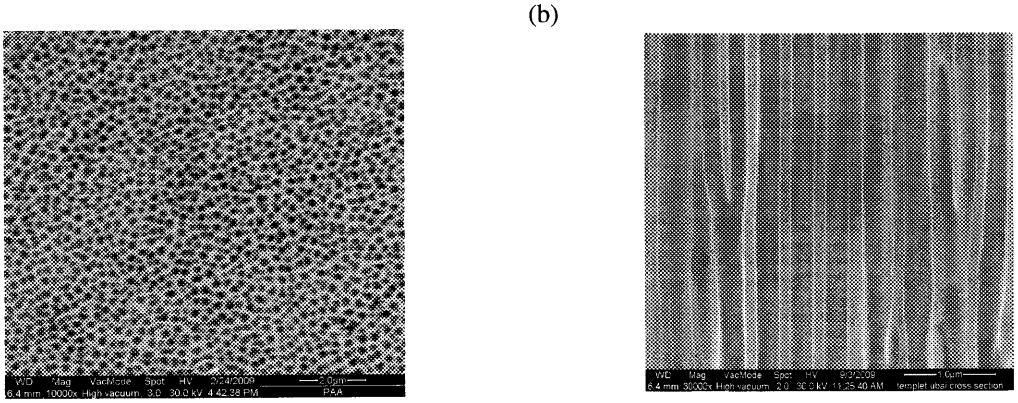

Figure 1. SEM micrographs showing (a) plan view and (b) cross section of the bare AAO template.

RESULTS AND DISCUSSION

Figure 2 shows the SEM micrographs of nickel nanowire arrays and free standing nanowires after removal of the template. Deposition of nickel nanowires started at the seed layer at the bottom of the pores of AAO template, followed by nanowire growth along the pore wall until the top of the template. The deposition occurred along the pore's wall surface due to the large surface area available as the energetically favorable sites for the adsorption of the nickel ions from the electrolyte which were then reduced to form nickel deposit (Cao et al., 2006). The nickel nanowires in the AAO template orientated nearly perpendicular to the membrane surface with uniform heights, indicating uniform nickel nanowire growth in each pore of the AAO template. Once the pores were completely filled with nickel, further electrodeposition produced hemispherical caps on the AAO template, which subsequently merged together to form continuous overgrowth film (Figure 3).

(a) (b)

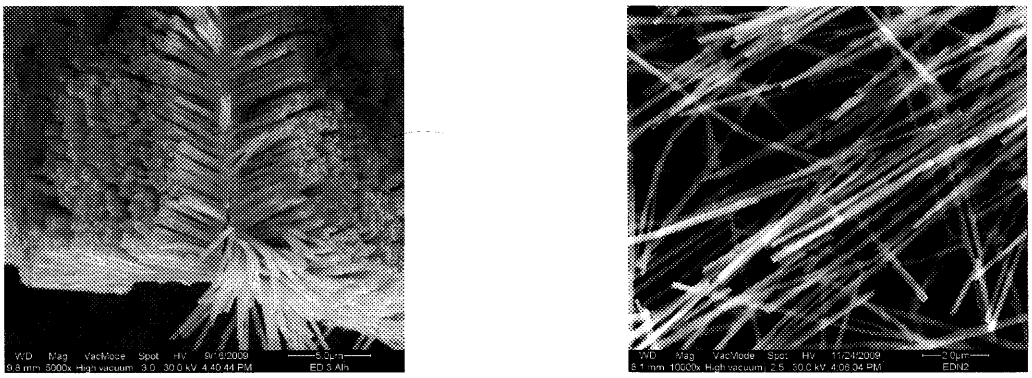

Figure 2. SEM micrographs showing (a) nickel nanowires arrays with partially dissolved AAO template and (b) free standing nickel nanowires after complete removal of seed layer and AAO template.

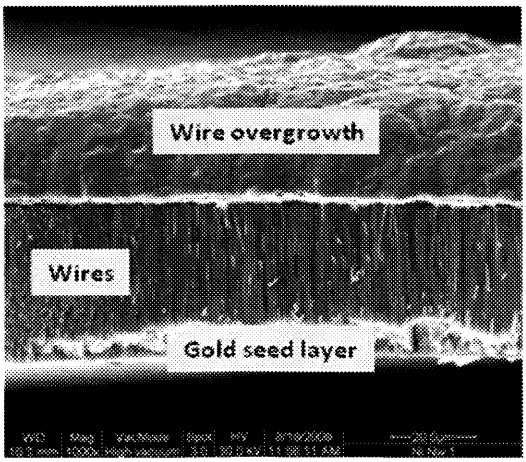

Figure 3. SEM micrograph showing thick nickel overgrowth on AAO template

Single nanowire alignment was performed using magnetic assembly technique on silicon substrate patterned with parallel gold electrodes of 3 μm gap size. Individual nanowire was positioned across the microfabricated gold electrodes in an external magnetic field provided by a pair of permanent magnets. Fig. 4 shows the schematic illustration of the assembly process. A 2 μl solution containing nickel nanowires was dispensed on the gap between the gold electrodes [Figure 4(a)]. Nickel nanowires, having magnetically easy axis parallel to the nanowire axis because of comparably stronger shape anisotropy than crystal anisotropy, preferably aligned across the gold electrodes in a direction dictated by the interactions between the nanowires and the external magnetic fields [Figure 4(b)]. When the length of the nickel nanowire was more than or equal to the gap distance between the gold electrodes, the nanowire aligned on top of the electrodes. Figure 5 shows the SEM image of a single nickel nanowire bridging the gold electrodes.

(a) (b)

Figure 4. Schematic illustration of the magnetic assembly of nickel nanowires

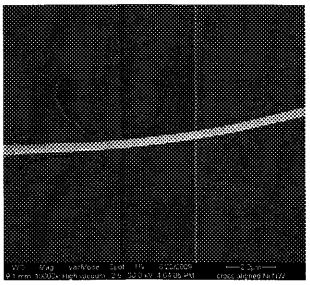

Figure 5. SEM image of a magnetically aligned nickel nanowire on the gold electrodes.

Figure 6 shows the x-ray diffraction patterns of nickel nanowires embedded in AAO templates. The nanowires were polycrystalline with face-centered cubic structure as shown by the presence of three different peaks close to 2theta angles of 44.5°, 51.8° and 76.4°, corresponding to Ni (111), Ni (002) and Ni (220) diffractions respectively. Preferred orientations of the nanowires relied upon the types of electrolytes used as well as the current densities during deposition. Nickel nanowires deposited with chloride bath have preferred orientation along the [111] direction for all pH values, whereas those deposited with sulphate bath of pH 1 and 2 have preferred orientation of [111] but were randomly oriented for pH 3 as may be evident from Figure 6. Nickel nanowires deposited with chloride bath using 10 mA cm^{-2} and 50 mA cm^{-2} current densities were preferably oriented along [111] but were randomly oriented when a current density of 1 mA cm^{-2} was used. It has been reported that if the deposition potential is much greater than the redox potential of nickel, [220] tends to be the preferred orientation for nickel nanowires deposition (Pan et al., 2005). However, a preferred orientation along [220] was only found in nickel nanowires deposited using chloride bath with current density of 1 mA cm^{-2}. This strongly suggests that the preferred orientation of the nickel nanowires was not only governed by the electrolyte conditions used, but also affected by the current density during deposition.

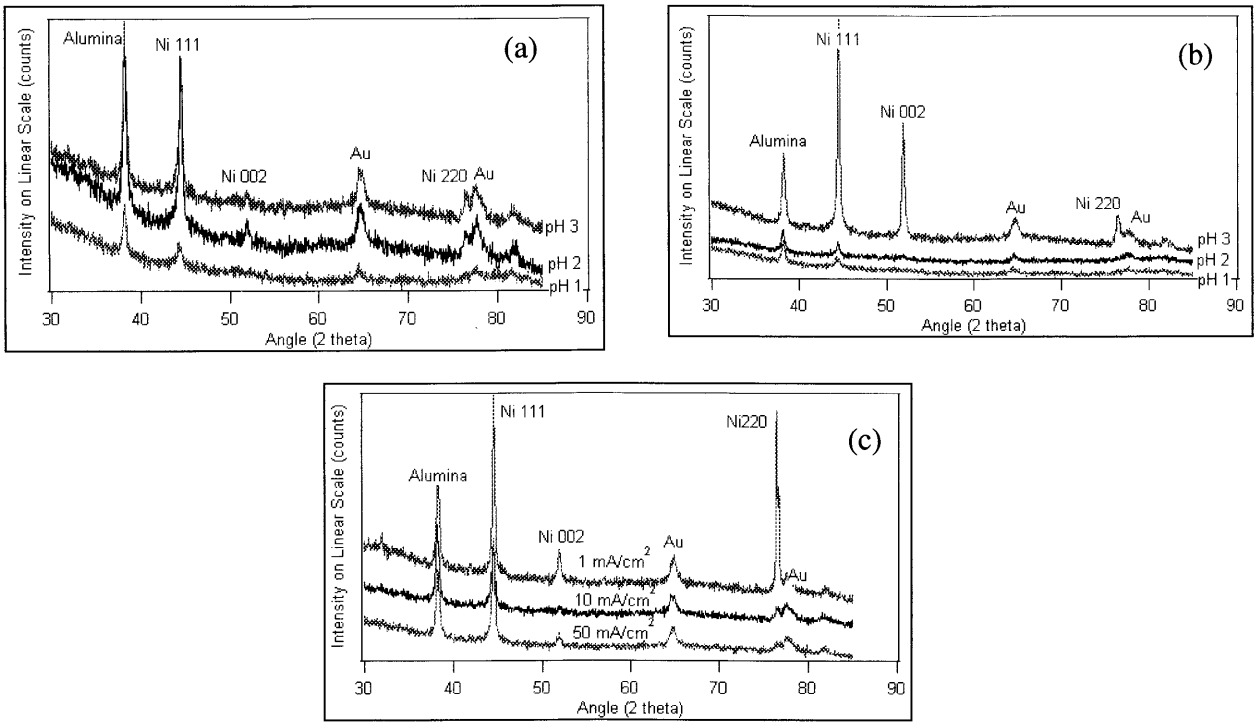

Figure 6. XRD patterns of nickel nanowires in AAO templates: (a) chloride bath of varying pH, (b) sulphate bath of varying pH and (c) chloride bath of varying current densities.

CONCLUSION

Nickel nanowires have been successfully synthesized via template directed electrochemical deposition technique. While the growth rates of nanowires were found to be increased with increasing pH values of the electrolytes, higher growth rate was also observed for chloride bath as compared to sulphate bath. The orientations of the electrodeposited Ni nanowires were also significantly governed by the deposition current densities and electrolyte conditions used. Magnetic alignment of single Ni nanowires between prefabricated gold electrodes for device structure also has been successfully demonstrated.

ACKNOWLEDGEMENTS

This work was supported by MOSTI (Science fund project No. 03-03-01-SF0030). The authors would like to acknowledge Pn Zaiton Selamat for her contributions in SEM work.

REFERENCES

Cao, H., Wang, L., Qiu, Y., Wang, G., Zhang, L. and Liu, X., (2006), Generation and growth mechanism of metal (Fe, Co, Ni) nanotube arrays, ChemPhysChem **7**. 1500 – 1504.

Hotový, I., Huran, J., Spiess, L., Capkovic, R. and Hascık, S. (2000), Preparation and characterization of NiO thin films for gas sensor applications, Vacuum 58, 300 – 307.

Masuda H. and Fukuda K. (1995), Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina, J. Science, 1466 – 1468.

Matsumiya, M., Qiu, F., Shin, W., Izu, N., Murayama, N. and Kanzaki, S. (2002), Thin-film Li-doped for thermoelectric hydrogen gas sensor, Thin Solid Films 419, 213– 217.

Neubecker, A., Pompl, T., Doll, T., Hansch, W. and Eisele, I. (1997), Ozone-enhanced molecular beam deposition of nickel oxide (NiO) for sensor applications, Thin Solid Films 310. 19 – 23.

Pan, H., Sun, H., Poh, C., Feng, Y. P. and Lin J. Y. (2005). Single-crystal growth of metallic nanowires with preferred orientation, Nanotechnology 16, 1599 – 1564.

Pirota, K. R., Navas, D., Velez, M. H., Nielsch, K. and Vazquez, M. (2004), Novel magnetic materials prepared by electrodeposition techniques: Arrays of nanowires and multi-layered microwaves, J. Alloys Compd. 369, 18 – 26.

Rabin, O., Herz, P. R., Lin, Y., Akinwande, A., Cronin, S. and Dresselhaus, M., (2003), Formation of thick porous anodic alumina films and nanowire arrays on silicon wafers and glass, J. Adv Funct Mater, 13, 631 – 638.

Rahman, I. Z., Razeeb, K. M., Kamruzzaman, M. and Serantoni, Md., (2004), Characterization of electrodeposited nickel nanowires using NCA template, J. Mater. Process. Technol. 153, 811 – 815.

Sun, X., Xu, F, Li, Z., Zhang, W., (2005), Cyclic voltametry for the fabrication of high dense silver nanowire arrays with the assistance of AAO template, J. Mater Chem Phys, 90, 69 – 72.

Xue, S., Cao, C. and Zhu, H. (2006), Electrochemically and template-synthesized nickel nanorod arrays and nanotubes, J. Mater. Sci. 41, 5598 - 5601.