

Electrodeposition of Ni micro/nano-structures

NIU LianPing^{1*}, YE DanDan¹, LI Feng¹ & ZHANG MingZhe²¹ College of Mathematics, Physics and Information Engineering, Jiaying University, Jiaying 314001, China;² National Laboratory of Superhard Materials and Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China

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A quasi two-dimension electrodeposition method was used to prepare materials with arborized, tree-shaped, and membrane patterned micro/nano-structures. The morphology of the membrane patterned micro/nano-structure was characterized using scanning electron microscopy, and a mechanism for the morphology formation was suggested. The novel preparation method used in this study, which is proprietary to our research group, does not require a template and so has many advantages including controllable, low cost, large scale preparation. The electrolyte concentration and electrodeposition voltage had a significant effect on the resulting morphology.

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Micro/nano-structures have attracted much recent attention because of their electrical [1], optical [2], chemical [3], catalysis [4] and magnetic [5,6] properties. They have potential applications in micro/nano-electronic devices, sensors and high density magnetic recording devices [7–10]. Ni is a useful magnetic material with unique properties. The highly ordered magnetic structure of Ni can induce outstanding cooperative phenomena that differ from the bulk and thin film analogs, and Ni micro/nano-structures have been extensively investigated [11]. Much research has focused on studying the characteristics and applications of Ni micro/nano-structures [12–20]. However, for such devices to be designed and applied, Ni micro/nano-structured materials must first be prepared. Vazquez et al. [21] fabricated arrays of Ni nanowires in alumina membranes, and studied the magnetic properties and interactions which influenced spatial ordering. Ohgai et al. [22] also studied Ni nanostructures, in which a polycarbonate film was irradiated with high energetic heavy ion beams to form straight tracks perpendicular to the film. Films were subsequently selectively etched to create cylindrical nanochannels where Ni nan-

owires were electrodeposited, and their anisotropic magnetoresistance (AMR) behavior was investigated. Narayanan et al. [23] fabricated Ni nanowires using template assisted electrodeposition, and studied the nanowire growth mechanism and magnetization behavior. Bentley et al. [24] prepared Ni nanowires using a template synthesis technique and characterized the nanowire properties. The alignment and movement of the nanowires could be controlled magnetically. Liu et al. [25] prepared Ni nanowires without a template using a magnetic field. Wang et al. [26] prepared Ni nanowires by a soft template method in ethylene glycol. Most of these reports involve templates being introduced to fabricate micro/nano-structures. While this method is very effective and the size and ordering can be controlled, templates must first be made from complicated and costly procedures.

In the current paper, chemical electrodeposition [27–33] without templates is used to prepare micro/nano-structures. Under an applied external voltage, solution phase metal ions are reduced to form deposited layers. When a voltage is applied across an electrode, metal atoms of the anode lose electrons to become cations, which then proceed into the electrolyte solution. Cations in the electrolyte move towards

*Corresponding author (email: nlpxy@126.com)

the cathode due to the electric field, where they then gain electrons. Lost electrons flow out of the anode and proceed back to the positive electrode via the electrical circuit, and then proceed to the cathode. A current circuit is formed depending on the movement of cations and electrons, and the metallic material can then be electrodeposited. Micro/nano-structure electrodeposition generally includes two processes, one forming the crystal nucleus and the other being the growth of that nucleus.

1 Materials and methods

NiCl₂ solutions with concentrations of 10, 30, 40, 50 and 80 mmol/L were prepared. Two Ni electrodes were fabricated, each being 30 mm long, 5 mm wide and 0.07 mm thick. Two Ni electrodes with wires were placed parallel to each other on 5 cm × 5 cm clean silicon substrate. Two or three drops of NiCl₂ solution were placed on the silicon substrate between the two electrodes, and with the electrodes and solution; then covered with a glass slide. The distance between the two electrodes was approximately 2 cm. Figure 1 shows the system comprised of electrodes, silicon substrate and electrolyte solution.

The next step was to fabricate an ultrathin liquid layer of NiCl₂. According to the principle of solute respective solidification, when the temperature decreases, the NiCl₂ electrolyte solution will freeze. The NiCl₂ solute would then separate from solution and reside between the ice and Si substrate layers, thus forming an ultrathin solute layer. Thus, the NiCl₂ solution was effectively localized into a two dimensional field, and when deposits grew in a single plane then ordered structures could be prepared. The power source was supplied by a function signal generator, with a constant voltage used to drive the electrodeposition and initiate the material preparation. Material growth was monitored using an optical microscope. The voltage was adjusted as necessary to control the growth speed and morphology.

2 Results and discussion

2.1 Characterization of arborized and tree-shaped Ni micro/nano-structures

Three different shaped micro/nano-structures were obtained from the electrodeposition experiments. Figure 2 shows

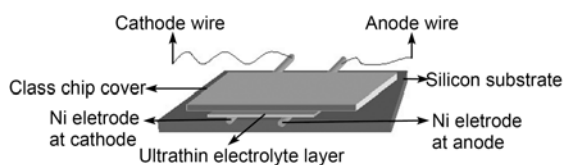


Figure 1 Schematic diagram of the preparation equipment comprised of electrodes, silicon substrate and electrolyte solution.

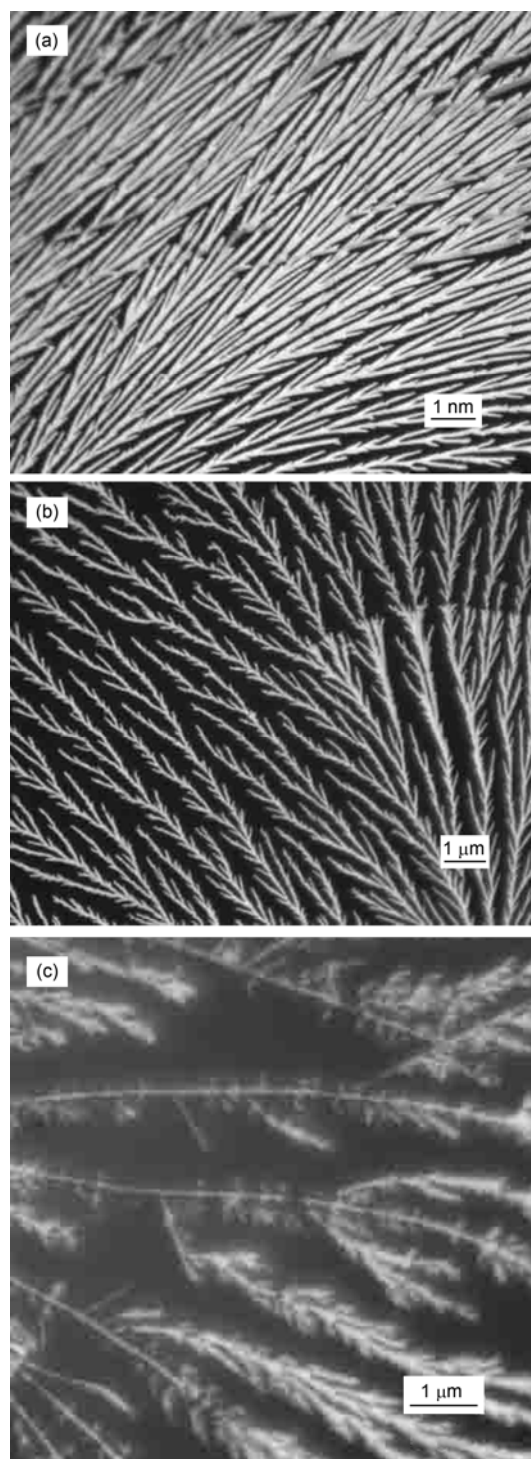


Figure 2 Optical microscope images of arborized Ni micro/nano-structures. Electrolyte concentration, applied voltage and pH were: (a) 10 mmol/L, 1.1 V, and 1.95; (b) 30 mmol/L, 1.4 V, and 1.90; (c) 40 mmol/L, 1.5 V, and 1.80.

arborized structures, of which three types were observed. The first type was distributed densely and single 'trees' contained few bifurcations, as shown in Figure 2(a). The second was distributed more sparsely but single 'trees' contained many bifurcations, as shown in Figure 2(b). The third

was distributed very sparsely and single 'trees' were more spinous, as shown in Figure 2(c). These results show that when the electrodeposition voltage and electrolyte concentration were higher, the resulting micro/nano-structures were more bifurcated. Overall, micro/nano-structures of sparse or linear arrays were easily formed. The thickness of the ultrathin liquid layer can also affect resulting morphology, because a thinner layer leads to more regular and well-proportioned deposition.

Tree-shaped Ni micro/nano-structures are shown in Figure 3, in which the trunks are straight. While individual 'trees' were sparse, single 'trees' exhibited many forks.

A mechanism for the electrodeposition procedure giving the above morphologies is suggested below. A lower concentration electrolyte was used to prepare the above samples. During electrodeposition, electrons were distributed from the head of the Ni sample. When electron distribution was constant thus achieving an equilibrium supply and consumption, Ni deposition did become bifurcated.

When the applied voltage was increased, the equilibrium between the supply and consumption of electrons was perturbed, leading to an increase in over potential and increase in deposition rate. If electrons were still in surplus in addition to consumed electron due to growth, electrons in the head of the deposition would continue to accumulate with further growth, and when this accumulation reached a certain level then repulsion between electrons would occur. In this situation, electron distribution would no longer be equal. Electrons that were confined at the head of the deposit would move toward the alternative end to minimize this repulsion. Two electron areas were formed, and when transported Ni^{2+} arrived at these areas, Ni^{2+} was reduced and bifurcation occurred as shown in Figure 4.

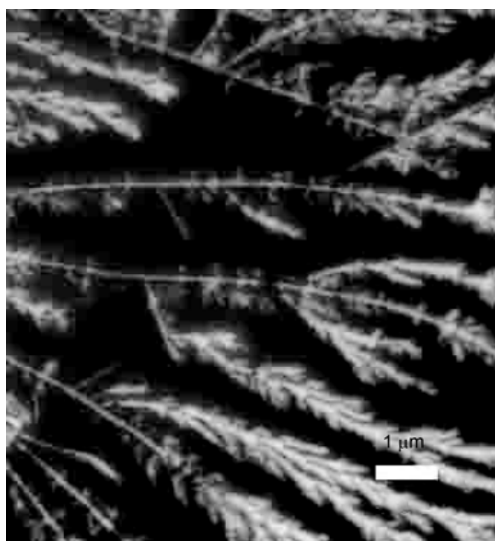


Figure 3 Optical microscope image of a tree-shaped Ni micro/nano-structure. Electrolyte concentration, applied voltage and pH were 50 mmol/L, 1.8 V and 1.62, respectively.

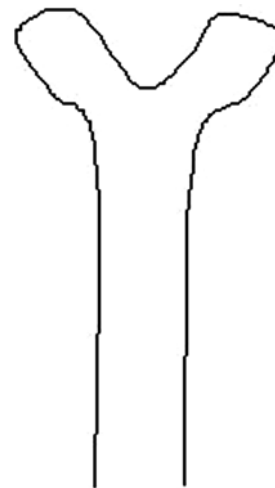


Figure 4 Schematic diagram showing bifurcation of a deposit.

If the applied voltage was lower, surplus electron density was lower and electron repulsion was weaker. Thus, the distance between electrons at the head of the deposit was less and growth was slower. The deposit bifurcated to a lesser degree giving a denser deposit, as shown in Figure 2(a). If the applied voltage was increased, surplus electron density was greater and electron repulsion was stronger. The distance between electrons was greater and the growth faster quicker. The deposit bifurcated to a greater degree giving a more sparse deposit, as shown in Figure 2(b). When the applied voltage was significantly increased, surplus electron density was very high and electron repulsion was very strong. The distance between electrons was very large and the growth was rapid. The deposit bifurcated to a very high degree, as shown in Figure 2(c). The different micro/nano-structures reported above are important for understanding the mechanism of crystal growth and also the possible uses of the materials. Arborized structures are more ordered and can be made over a larger area, thus could be applied in ultrahigh density magnetic storage devices. The recording densities of such devices will be much higher than those obtained from conventional continuous magnetic films.

2.2 Characterization of membrane patterned Ni micro/nano-structure

The membrane patterned Ni micro/nano-structure is shown in Figure 5. Figures 5(a) and (b) are images of a single sample but at different magnifications. Arrows indicate the growth orientation of the material which is aligned with the applied electric field. Figure 5(a) shows an obvious periodic morphology and a smooth membrane surface. Figure 4(b) shows that the membrane had a vivid interface between periods, and that the period length was $\sim 2 \mu\text{m}$.

The membrane was easily prepared by electrodeposition under the conditions of high electrolyte concentration

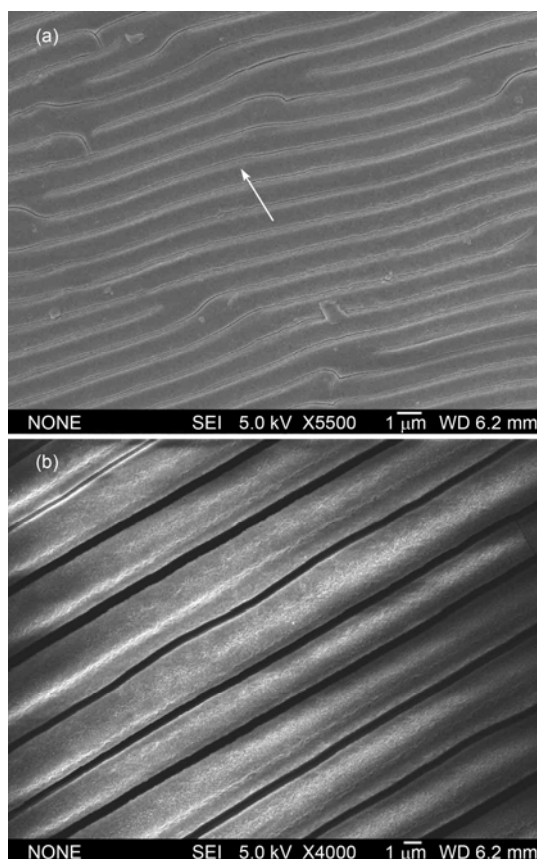


Figure 5 SEM images of the membrane patterned Ni micro/nano-structure. Electrolyte concentration, applied voltage and pH were 80 mmol/L, 4.0 V and 1.53, respectively.

(>50 mmol/L) and voltage (>4 V), but the growth process was slow. In preparing Ni micro/nano-structures, the predominant chemical reaction is the reduction of Ni^{2+} to Ni at the cathode. The reaction equation is $\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$. Reduced Ni^{2+} initially formed crystal nuclei and those nuclei grew into the above Ni micro/nano-structures.

A mechanism for the electrodeposition of the membrane is suggested below. A high concentration electrolyte was used, and the applied potential corresponded to the electrolyte concentration. During electrodeposition, a small potential relative to the electrolyte concentration resulted in a slow growth speed. Electrons had sufficient time to migrate upon repulsion, in the direction parallel to the electric field, and thus were uniformly distributed in one plane. The distance between two neighboring electrons was relatively close following their rearrangement for repulsion. When Ni^{2+} arrived at the surface, Ni^{2+} was reduced and the Ni structure grew. If electrons were stoichiometrically consumed during reaction then there was no surplus electron density. The transportation of Ni^{2+} and consumption of electrons by reduction achieved equilibrium, resulting in deposition of a membrane structure but without a period. If electrons were in surplus, then the potential of the cathode would become more negative. The over potential of the

cathode would increase, thus the speed of transportation and reduction of Ni^{2+} would also increase leading to electron depletion at the cathode. Reduction ceased at the cathode when the over potential decreased to zero. When the cathode became charged following the arrival of Ni^{2+} , the electrode potential increased, the cathode over potential was again present, and thus reduction occurred again. The process repeated to form an undulated structure with over potential. When over potential was present the reaction proceeded. When over potential was lower than the reduction potential the reaction paused. The resulting membrane had a periodic structure as shown in Figure 5.

3 Conclusions

Three different Ni micro/nano-structures were prepared. The morphology of the resulting structures could be controlled by adjusting the electrodeposition conditions. It was easier to fabricate ordered patterns at lower applied voltages and electrolyte concentrations, which is important for the electrodeposition process. Our results provided theory related to chemical electrodeposition supported by experimental data, and will be important for the future development of micro/nano-structures materials. The prepared structures had unusual morphologies that have potential applications in micro/nano-devices.

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