Electrodeposition of Micro-Nanostructured Nickel Film on Flexible Substrates

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Abstract

High surface area nickel such as porous nickel has been found advantages for being utilized in electrochemistry applications. However, conventional fabrication technique is template-assisted in which template material is consumable contributing to production cost, especially in the case of nanoscale featured nickel. Here, we proposed a template-free fabrication technique for micro-nanostructured nickel film on a flexible substrate based on wet chemical and electrochemical surface finishing. Thin nickel film was electroplated on an aluminum foil substrate precedingly coated with a layer of zinc microcrystal. Multiscale structured nickel film was achieved in which nickel particles with a few hundred-nanometer diameter were featured on the microstructured underlayer. The electroplated nickel film was crystalline and highly orientated in [111] direction. Enhancement of light trapping and an increase in hydrophobicity after stearic acid treatment were observed, attributed to the presence of micro-pore in the structured film. The presented fabrication technique for high surface area nickel film is ease to scale up and could be useful for mass-production of a nickel-based functional device.

Keywords: Electroplating: Nickel: Micro-nanostructured film: Flexible substrate

Introduction

Nickel and its compound such as oxide and hydroxide are typical materials in electrochemistry due to their stability to redox reaction, good electrical conductivity and ease of processing. Fabrication of nickel to be a form having high surface to volume ratio such as nickel foam has extended implementation of nickel to variety of research topics and applications [1]. Conventional method to fabricate such material is to electroform nickel onto a skeleton template which is subsequently removed at the end of the process leaving a 3D interconnected network of nickel [2]. The same principle was derived for microscale structure in which anodic aluminum oxide and self-assembly microsphere have been frequently used as a template [3]. However, mass production of those microscaled materials is found in difficulty such as technique and cost for scaling size of a template up. Although, it is feasible to produce microstructured nickel in cone shape without templating [4], an additive which is used to stimulate crystal growth in a specific direction is expensive. In this paper, we present fabrication of a micro-nanostructured nickel film on an aluminum foil by utilizing simple electroetching and plating technique. The technique is template-free and capable of producing semi-porous nickel film in which unique morphology and properties arose from the structured surface were characterized.

Materials and Methods

Sample preparation was performed in a series of process steps including cathodic etching of an aluminum substrate, double zincate and nickel plating. A substrate was a cleanroom aluminum foil supplied by All Foils, Inc. The foil was approximately 25 micrometer thick and laminated with a plastic sheet to make a support and also to protect the bottom side of an aluminum substrate from contacting to an electrolyte. A substrate was rinsed with isopropanol and deionized water before being cathodic etched to roughen the surface of a substrate. An etching solution was 3 vol % hydrochloric acid. Etching duration was for 30 seconds with current density of 1 A/dm^3 counter to a graphite anode at electrolyte temperature of 80 ºC and a substrate was then rinsed with deionized water. In the next step, double zincate pretreatment was used to coat a zinc layer on a rough aluminum substrate. A zincate solution was a mixture of 100 g/l zinc oxide and 500 g/l sodium hydroxide solution in deionized water. A 5 vol % nitric acid solution was used as a zinc stripping. In the first zincate, a substrate was immersed in a zincate solution for 30 seconds, followed by dipping in striping solution to remove the deposited zinc layer. A sample was then immersed in a zincate solution for the second time for another 30 seconds and rinsed in deionized water. In the last step, nickel film was electroplated on a double zincated aluminum substrate in a Watts plating bath. Watts plating solution contained 260 g/l nickel sulfate ($NiSO_4$), 40 g/l nickel chloride ($NiCl_2$) and 40 g/l boric acid (H_3BO_3) in deionized water. The final pH value was 3. Nickel was deposited at current density of 1 A/dm^3 counter to a nickel anode bar for 5 minutes at room temperature. The nominal film thickness was calculated to be 1 micrometer at the current efficiency of 100%. A control sample was prepared using the aforementioned process without cathodic etching for comparison. The surface morphology and elemental composition were investigated using a Hitachi S3400N scanning electron microscope integrated with a Horiba EMAX energy-dispersive x-ray fluorescence analyzer. Crystal structure was characterized using a Bruker D8 Advance 2-theta x-ray diffractometer equipped with Cu K-alpha radiation source. Reflectance of a coated nickel film was measured using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Contact angle experiment was performed to compare hydrophobicity of nickel films after surface modification by soaking a sample in 10 g/l stearic acid in ethanol for 1 hour and drying in air.

Results and Discussion

Surface of an aluminum foil substrate was initially flat. It became rugged after deposition of zinc and then nickel. The control nickel electroplated sample was dull and grainy, which is typical for a Watts plating bath without addition of brightener or leveling agent; however, highly structured surface is hardy achieved. In Figure 1, top-down SEM images of a sample at each step during fabrication of a micro-nanostructured nickel film. After cathodic etching in an acid solution, aluminum surface posed corrosion pits with pore size in the order of several micrometers as shown in Figure 1 a). This surface pitting is due to preferential etching of an acid to [100] direction of aluminum. Surface roughening is believed to be a crucial step to prepared micro-nanostructured nickel film as the rough surface promote growth of zinc microcrystal array on aluminum surface during a double zincate step. Zinc microcrystals were arranged to expose their edges and corners upright causing a corrugated surface substrate as shown in Figure 1 b). Morphology of the nickel coated film is shown in Figure 1 c). The film morphology was hierarchical combining nanoscale and microscale structures. There were nanodots with size randomly between 100 and 500 nanometers decorated on array of microislands with size approximately a few micrometers. It has been well-known for electroplating that metal ions tend to deposit and grow rapidly at a position having high electric flux typically at the apex resulting in a bumpy structure. In addition, the microisland feature was derived from structure of an intermediate layer made of zinc microcrystal.

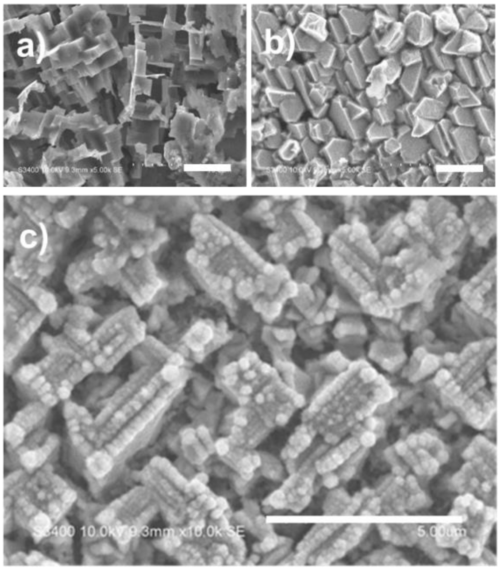

Figure 1 SEM images for a) cathodic etched aluminum surface, b) double zincate on a sample in a), and c) semi-porous nickel on the top layer. A scale bar is 5 micrometers.

Elemental compositions of the nickel plated film are shown in Table 1. The film composed of nickel as the majority element and other metals such as iron and copper presented as impurities in the plating bath. Zinc and aluminum signal could be generated from elements at the bottom layer.

Table 1 Element composition of the nickel plated sample.

Element	Ni	Zn	Fe	Al	Others
Weight %	91.2	3.6	0.2	0.2	4.8

Figure 2 shows 2-Theta x-ray pattern of the nickel film. There was the only one principle peak assigned to (111) reflection of cubic structure indicated that the nickel film was crystalline with highly oriented in [111] direction. The results were similar to that of the control film. Structure of other trace elements or their alloy with nickel was not observed. Therefore, those elements possibly existed in an amorphous form.

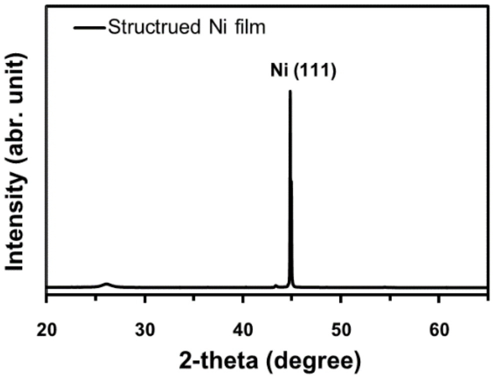

Figure 2 2-Theta x-ray diffractogram of the structured nickel film

Reflectance of the film surface was measured. The control sample appeared to be dull and grayish with an average value of reflectance about 30% over visible region. In the other hand, the micro-nanostructured nickel film was darker and its reflectance value was 17%. The decrease in reflectance could be that the micro-nanostructure promotes multiple reflection inside the micro-pore and enhance total light absorption. It is reasonably that such structure is the origin of dark colored film in addition to the intrinsic absorbance of nickel.

Contact angle measurement was used as an indirect method to evaluate porosity of the structured surface. Surface of the electrodeposited nickel was modified with stearic acid to form hydrophobic layer. Contact angle of a drop of deionized water on the surface was measured for the micro-nanostructure film and the control sample. It was found that the contact angle was 134° for the micro-nanostructure sample, greater than that of the control sample which was 105°. It is believed that an increase in hydrophobicity could attribute to hierarchical micro-nanostructured surface posing large interface area as suggested in a previous review [5].

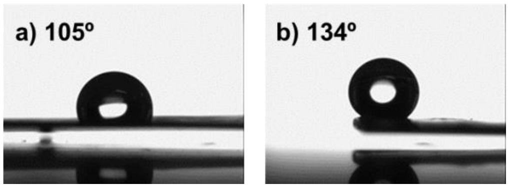

Figure 3 Photographs and contact angle values of a water droplet on a) the control sample and b) the structured nickel.

Conclusions

The method to coat micro-nanostructured nickel film on a zincated aluminum foil based on convention surface finishing technique was presented. Growth of nickel nanoparticles on a microstructed underlayer is the major key for this design. The nickel film posed semi-porous structure guiding to large surface area; in conjunction with a flexible and electrically conductive substrate, it may provide a potential platform in electrochemical, gas sensing and catalyst applications.

Acknowledgments

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