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Fabrication of nanopatterned metal sheet using photolithography and electroplating

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ABSTRACT

This paper describes a technique for fabricating submicron nickel (Ni) structures on flexible metal substrate. Conventional photolithography and electroplating techniques are used for simple and cost-effective fabrication of size-tunable Ni nanostructures. In the photolithography process, to separate the substrate and metal layer, a residual layer was intentionally preserved when patterning the thick photoresist layer. Then, the Ni seed layer was deposited on the photoresist pattern. By applying pulse electroplating to the seed layer, a Ni metal layer was formed on the seed layer. As a result, a nanopatterned Ni metal sheet was easily obtained using the photoresist strip process. Then, the Ni nanopattern was transferred onto a flexible polycarbonate substrate. In addition, various energy-controlled exposures of the resist were demonstrated for fabricating size-tunable Ni nanostructures, by simply removing the intentionally induced residual layer of the resist pattern. This research is adaptable for the fabrication of various sensor applications and energy storage devices.

1. Introduction

Recently, flexible devices have been widely researched in the field of bio-sensors, gas sensors, and energy storage devices, as well as optical and touch devices [1–5]. The flexible devices in those fields are generally implemented using printed circuit board, electronic chips, and electrodes because they provide flexibility as well as good productivity, stability and durability.

In particular, flexible, nanopatterned substrates enable the use of such flexible components in high performance electronic devices. For instance, nanopatterned metal electrodes are applicable for solid-state capacitors, which improve energy storage density by increasing the reactive area [6]. Also, a bio-sensor made with flexible nanopatterned metal electrodes can detect an enzyme by modifying pattern period and size [7]. For applications such as these, a number of patterning methods have been developed (*e.g.*, electron beam lithography, photolithography, nanoimprint lithography, and block-co-polymer) [8–11]. Although electron beam lithography and photolithography are now conventional technology for fabricating electronic devices, these techniques have limitations for patterning flexible substrates because of focus mismatching. Nanoimprint lithography provides a simple build-up process of a nanopattern on a flexible substrate, and it is a feasible technique for mass production using a continuous roll-to-roll process. However, there is a problem with the durability of the imprint stamp that must be overcome. A patterning method using block-co-polymer or nanoparticles enables fabrication of small nanopatterns. Also, these bottom-up methods are simple and inexpensive methods for fabricating over large areas. On the other hand, patterning of specific shapes is not supported by the bottom-up method. Therefore, a hybrid patterning method is required [12].

In this study, a patterning method was developed on flexible metal sheet using photolithography and an electroplating process. To fabricate a photoresist pattern, conventional photolithography was applied to a silicon substrate using a KrF excimer laser stepper. At this stage, the photoresist was thickly coated in order to form a residual layer on the substrate. This residual layer enables easy detachment of both substrate and metal sheet after the electroplating process. In this experiment, a Ni seed layer was deposited by an electron beam (e-beam) evaporator for the electroplating process. Then, the electroplating process was applied to the substrate. The photoresist was simply removed by dipping into an organic solvent. As a result, a nanopatterned metal sheet was obtained. We demonstrated a nanopatterned metal sheet appropriate for use as a flexible Ni stamp of the sort used for nanoimprint lithography.

2. Experimental details

A 6 inch bare silicon wafer was prepared, and the substrate cleaned with piranha solution ($H_2SO_4 : H_2O_2 = 4 : 1$) at 110 °C for 10 min. To remove the native oxide layer, the substrate was dipped into diluted hydrofluoric acid (HF : Distilled water = 1 : 100) solution for 1 min and then cleaned with pure distilled water. Then, the silicon substrate was dried with nitrogen gas. To improve adhesion between the photoresist and silicon substrate, hexamethyldisilazane was sprayed on the substrate, and KrF photoresist (DJKI-2525, DongJin SemiChem, Korea) was spin coated at 500 rpm for 20 s. Subsequently, the substrate was baked on hot plate at 100 °C for 60 s.

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Table 1
Photolithography conditions.

Parameter	
Original pattern	350 nm hole, 2 μm pitch
Photoresist	DJKI-2525 (Dongjin SemiChem, Korea)
Substrate	6-inch Si (100)
Coating condition	500 rpm, 20 s
Soft baking	100 °C, 60 s
Exposure energy	30 mJ/cm^2 ~ 100 mJ/cm^2
Post exposure baking	110 °C, 60 s
Development	AZ300MIF, 60 s

Table 2
Electroplating conditions.

Parameter	
Current density	8.6 mA/cm^2
Seed layer	Ni 200 nm
Time	30 min
Rotation speed	10 rpm
Flow rate	10 ℓ/min
Duty ratio	70%

In this experiment, it was important to increase the pattern density on the flexible metallic substrate. Therefore, an exposure test was conducted to see the trend of pattern size and depth, using a KrF stepper (PASS5500/300C, ASML). Table 1 shows the detailed parameters of the photolithography process. The original test pattern was a periodic hole-pattern of 350 nm size and 2 μm pitch in wafer scale. The exposure energy was modulated from 30 mJ/cm^2 to 100 mJ/cm^2 without optimization of the focus. After the exposure was completed, post-exposure baking was done at 110 °C for 60 s. The development time was fixed at 60 s. The pattern shapes were examined using a Hitachi S-4800 field-emission scanning electron microscope (SEM) with an acceleration voltage of 15 kV. The electroplating process was performed after depositing a Ni seed layer of 200 nm thickness on the photoresist pattern using an e-beam evaporator. To improve adhesion, the substrate was treated with diluted sulfuric acid (H_2SO_4 : Distilled water = 1 : 10) for a few seconds. Table 2 shows the parameters of the electroplating process. The electrical current setting for the electroplating process was 1.5 A, and pulsed current was applied for 30 min. To increase the plating uniformity, the rotation speed of the plating jig was set to 10 rpm, and the solution flow rate was set to 10 ℓ/min. After the electroplating process, the photoresist strip process was conducted using ultrasonication in acetone.

Further experiments with the nanopatterned metal sheet were conducted to show its applicability for imprint lithography. Using the procedure just described, a 1.4 μm pitch, 1 μm height and 450 nm sized metal nanopattern was fabricated. Imprint resin (NIPSC28LV400, ChemOptics, Korea) was coated onto the flexible polycarbonate substrate by spin coating at 1000 rpm for 40 s, followed by transference of the nanopattern onto the polycarbonate substrate using UV imprinting for 2 min at 20 MPa. Finally, the nanopatterns were transferred by removing the metal sheet.

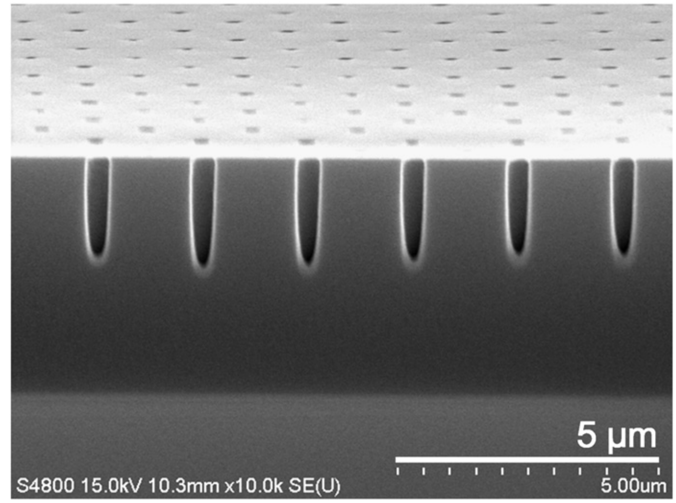

Fig. 2. Tilt-view SEM image of photoresist pattern. A residual layer was observed on the silicon substrate.

3. Results and discussion

Fig. 1 shows the overall fabrication processes to obtain a nanopatterned metal sheet using photolithography and electroplating. Both process steps are simple and suitable for mass production. The main advantage of this process is the ease by which the nanopatterned metal sheet can be detached from the substrate due to the residual layer of the photoresist pattern. To keep the residual layer of photoresist, the spin coating process was carried out at low rpm for only a short time. As shown in Fig. 2, periodic hole-patterns formed on the resist residual layer.

Generally, the major parameters of photolithography are exposure energy, focus, baking temperature, and development time. By modulating these parameters, various sizes and depths of the target pattern can be obtained. These parameters should be taken into account to develop the desired pattern. We modulated the exposure energy to control the diameter of the holes needed for fabricating the size-tunable Ni nanostructures. A split test of exposure energy was carried out on the thick photoresist. Fig. 3 shows the cross-sectional view and size transition of the photoresist pattern. In this test, the

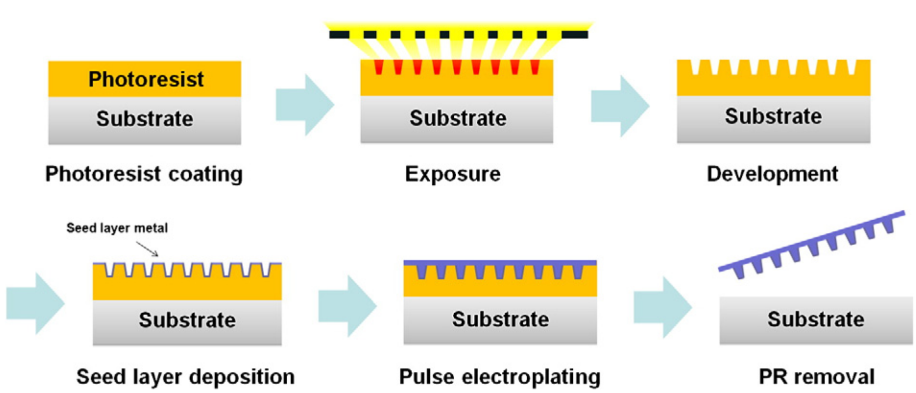

Fig. 1. Overall fabrication procedure of nanopatterned metal sheet.