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Flexible metal film with micro- and nanopatterns transferred by electrochemical deposition

Jun Feng *, Bo Cui, Yong Zhan, Stephen Y. Chou

Department of Electrical Engineering, Princeton University, NJ 08540, USA

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Abstract

A new method for patterning microstructure on metal film by electrochemical deposition is provided. The metal film with micropattern can be peeled off after the deposition by inter-medium layer of resistant molecules such as triglyceride. We can use the technology of electrochemical deposition to make the metal film possess different functions such as soft and bendable properties. We also give an example to get the protein pattern transferred on the metal film. So, this method can also provide a way for the fabrication of protein pattern on the chip. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Micro- and nanopatterns; Metal film; Peel off; Protein pattern

1. Introduction

Fabrication of micro- and nanostructures with high fidelity and low cost is an area that has attracted much interest during the past few years. Methods including self-assembly [1–7], imprint lithography [8–11], and microcontact printing [12–17], which also mainly developed with self-assembly technology, have been proposed in the process of searching new ways of fabricating high quality micro- and nanostructures. Much of these efforts have been expended on their organization on surfaces for the construction of functional interfaces, which have led to numerous sensing, electronic, optoelectronic, and photoelectronic interfaces [18]. Most of the structures are mainly patterned on silicon wafer that has hard and planar properties. Patterning micro- and nanostructures on flexible film is a new interesting area, which may provide nanopatterns on curved surface if the film can bend or even can roll up. Generally, the metal film can be produced by electroless deposition [19,20] or electrodeposition [21–24]. However, it is difficult to separate the film from the base the film deposited on. The traditional separation is to sacrifice the base by the etching method. In this paper, we reported a very simple method for the fabrication of soft metal films with patterned microstructures and even the protein structure, and then the metal film can be separated with the base spontaneously. Self-peeling off method for metal film has the advantage of not to sacrifice the template for the patterning. So, it may provide an economical and convenient route to multiple copies of the micro- and nanopatterns written on the master.

2. Experimental

2.1. Materials

The lead–tin soft metal film was chosen to make the micropattern. We added copper component in the film in order to increase the film's hardness. The electrolyte was composed of $Pb(BF_4)_2$, $Sn(BF_4)_2$, $Cu(BF_4)_2$, and HBF_4 (General Chemical, Parsippany, NJ 07054). The composition was: lead 80–90 g l^{-1}, tin 5–7 g l^{-1}, copper 2–2.3 g l^{-1}, free fluoroboric acid 150–180 g l^{-1}. In order to get the fine deposition, additives 0.2–0.4 g l^{-1} of gelatin and 2–4 g l^{-1} of phenol were added. Triglyceride was used as a resistance membrane material (Sigma-Aldrich product).

* Corresponding author. Address: University of California, Mechanical Aeronautical Engineering, 95616 Davis, CA, USA. Fax: +1-530-752 4158.

E-mail address: jfeng@ucdavis.edu (J. Feng).

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2.2. Deposition of lead–tin–copper metal film

A nickel film (25 mm × 30 mm × 2 mm) was chosen as master, which was cleaned by acetone, methanol and water washing and then treated by HCl (0.1 M) and by NaOH (0.1 M). Then the solution of triglyceride in acetone (1:1.5) was spread on the master by spinning it on. After the solution spinning and the acetone evaporation, the macromolecular membrane was formed on the template. Then, the deposition began at 1.2 A dm^{-2} of the current density. After several minutes, such as 5 min, the deposition rate increased to 2 A dm^{-2}. In about 40 min, 75 μm of the metal film was reached.

After the metal film was finished it was taken out, washed and dried by air. Then, the metal film was peeled off by cutting off the edge (Fig. 1).

2.3. Metal film with micro-, nanostructure and protein pattern

As described in Fig. 1, when the template has a certain pattern, the metal film by electrochemical deposition will have the pattern matched with that of the master. For the metal film with protein pattern, we used the nickel film spattered on silicon wafer. The pretreatment was the same as above. After the resistant film was formed on the nickel surface, the protein solution (gelatin: 10–15 g l^{-1} in water, the solution was prepared by the cold water swelling method) was dropped on it and was spread carefully. The protein membrane was formed after evaporating the solvent. Then the ''protein template'' was put into the electrolyte and the deposition was started as soon as possible. After the metal deposition and the peeling off of the metal film with the base, the film with the protein pattern was washed with acetone, methanol and water carefully to wash away protein molecules left on it.

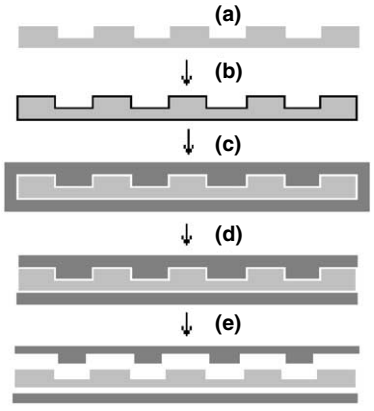

Fig. 1. Principle of micro- and nanostructure patterns on lead–tin–copper film transferred by electrochemical deposition. (a) Metal master; (b) the master with lipid membrane applied and dried; (c) electrochemical deposition; (d) making edge cut; (e) peeling off the deposition and the master.

3. Results and discussions

We present, here, a new possible methodology for the fabrication of metal film with micro- or nanostructure patterns by electrochemical imprint on a cathode template. The thickness of the metal film can be regulated by the deposition conditions. We can choose soft kinds of metals such as lead–tin alloy in this paper. We can also add some hard metal, such as copper, to increase its hardness. This patterned metal film has high quality of flexibility than silicon wafer and also can have relatively high resolution. Fig. 2(a) shows the SEM image of the electrochemically deposited lead–tin–copper film with a 20 μm period pillar array transferred onto it from the master. And Fig. 2(b) shows the AFM image of the deposited film with a 300 nm period grating structure on it. Lead–tin alloy has the high quality of flexibility. In developing micro- and nanopatterned metal film by

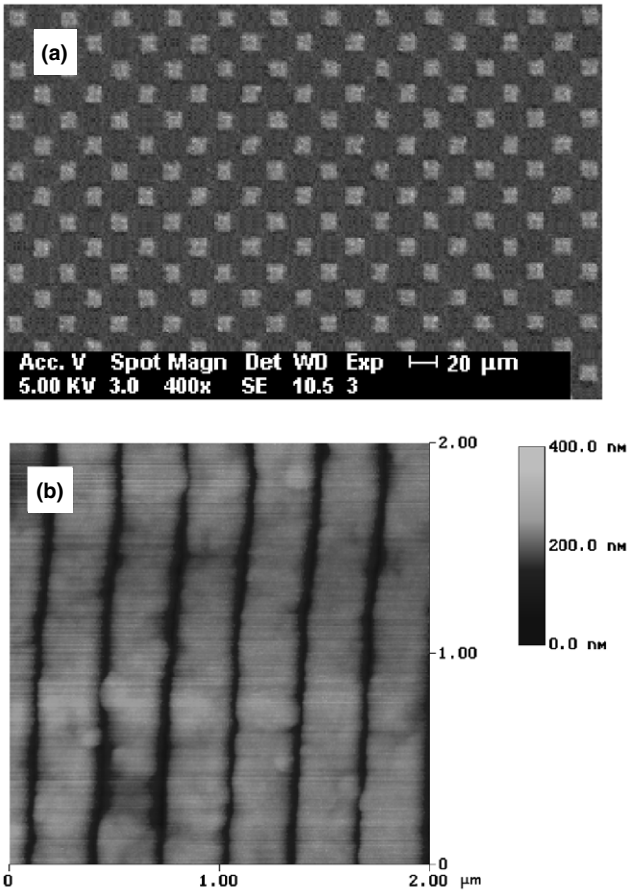

Fig. 2. SEM picture of the transferred microsquared pillar pattern (a, 20 μm) AFM picture of the transferred nanograting (b, 300 nm) on lead–tin–copper film.

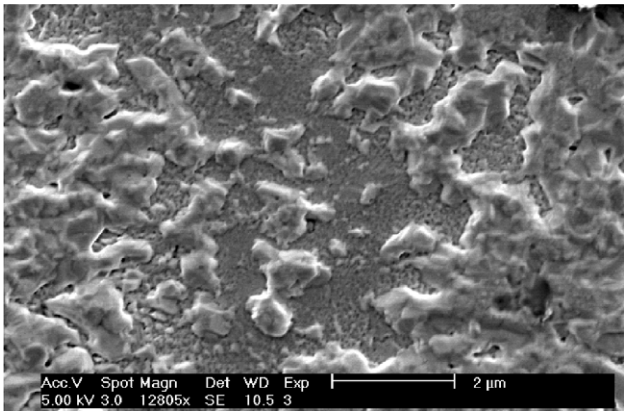

Fig. 3. SEM picture of the gelatin pattern transferred on lead–tin–copper film (100 μg ml^{-1} of gelatin in solution before the membrane on the master was formed).

electrochemical deposition technology, we can also make use of the electroplating knowledge to make the metal film having anti-corrosion, anti-erosion and anti-deformation. For example, the lead and tin components can make the film both soft and anti-corrosive, and the addition of copper can increase the hardness of the film. So, the metal film of lead–tin–copper has high quality of flexibility in bending. It can be made to a curved shape, does not break and has a certain hardness to maintain the pattern unchanged.

We developed the membrane peeling-off technology by spinning a thin layer of fat–oil between the template and deposition layer. This kind of thin layer made the peering off of the layer of the deposition from the base metal easy. However, this thin molecular layer was not harmful to the electrochemical deposition and had no influence on the micro-, nanopatterns transferred. In the aspect of replication in micro- and nanostructures, the self-peeling off method for metal film has the advantage of not to sacrifice the template for the patterning and may provide an easy way to multiple the copies written on the master.

Synthetic materials capable of selectively recognizing proteins are the areas having important biological significance [25–29]. Protein recognition is firstly attributed to the shape pattern transferred [28] and protein-imprinting technology may provide a way towards artificial antibodies [29]. In this experiment, we found that protein can be the template that can be used to get the protein pattern transferred on the metal film by the electrochemical technology. We chose gelatin to get the protein image pattern on the soft metal film. Fig. 3 is the result. We know that electrochemical deposition is a process based on the molecular level, macromolecules on the master physically induce the deposition according to the shape of the macromolecules and leave their pattern right in front of the metal surface. So, this result suggests that the patterned protein image technology may provide a way for fabricating the metal based protein antibody that will be significant in obtaining protein chip conveniently and also at low cost as well.

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