Direct Fabrication of Metal Patterns on Resin Substrate by Combining Imprint and Electrochemical Lithography

Yusuke KIMURA*, Ryosuke FUZIWARA, Takaaki TSURUOKA, Yohei TAKASHIMA, Hidemi NAWAFUNE, Hiroshi YANAGIMOTO and Kensuke AKAMATSU*

*Department of Nanobiochemistry, Frontiers of Innovative Research in Science and Technology (FIRST), Konan University (7-1-20, Minatojimaminami, Chuo-ku, Kobe-shi, Hyogo 650-0047)

We report a new patterning method to fabricate metal patterns on polyimide substrate with trench structure by combining imprint and electrochemical lithography. Using an ion-doped precursor polyimide films with trench structure prepared by imprint lithography, metal thin films can be successfully deposited at convex portion of trench structure through electrochemical and ion-exchange reactions, which resulted in the generation of metal patterns on polyimide films. The present process is quite simple, which can be performed without resist coating, exposure and etching. Therefore, the study provides effective methodology for fabrication of flexible printed circuit boards.

Keywords: Direct Metallization, Ion Exchange, Electrochemical Lithography

1. Introduction

Polyimide films have been widely used for flexible printed circuit board because of their excellent thermal stability, dielectric properties and mechanical strength. The conventional method to fabricate metal circuits on polyimide substrates utilizes lithographic methods. However, this method requires stringent environmental control, costly equipment, and complex multistep processes such as resist coating, exposure, and etching. Further, metal patterns obtained by conventional method suffer poor adhesion between metal and polyimide substrate when metal patterns are miniaturized. Therefore, the development of new methods that ensure miniaturization and higher adhesion between metals and substrate is challenging. In this study, we report a new patterning method to fabricate metal patterns on polyimide substrate with trench structure by imprint lithography combined with electrochemical lithography. Using an ion-doped precursor polyimide films with trench structure prepared by imprint lithography, metal thin films can be successfully deposited at convex portion of trench structure, which resulted in the generation of metal patterns on polyimide films. This method is a simple process without resist coating, exposure and etching and thus provides an effective methodology toward lower-cost and high-throughput microfabrication.

2. Experimental

Schematic of the present fabrication process is shown in Fig. 1. In the present study, poly (amic acid) (PAA) film was used as an ion-exchangeable precursor. The PAA is synthesized from pyromellitic dianhydride (PMDA) and a 4,4'-oxidianiline (ODA). N-methylpyrrolidone (NMP) solution of poly (amic acid) was spin-coated onto a silicon wafer with trench structure, followed by heat treatment in vacuum at 100 °C for 1 h (Fig. 1 a). Poly (amic acid) film with trench structure was obtained by peeling off from the silicon wafer. The obtained ion-exchangeable precursor films were immersed into a 200 mM aqueous solution of silver nitrate or copper sulfate for 1 h to dope the metal ions (Fig. 1 b), followed by washing with distilled water. After the ion exchange reaction, convex portion of poly (amic acid) film doped with silver ions was connected to the ITO substrate as a cathode, and a Pt substrate as an anode was placed onto the convex portion (Fig. 1 c).

Fig. 1 Schematic diagrams of (a) imprint lithography process, (b) ion-exchange reaction, (c) electrochemical lithography.
poly (amic acid) film (Fig. 1c). Before placing the Pt anode, a few drops of distilled water was coated onto the film surface by pipette, which accelerates the electrochemical reaction. The electrochemical deposition of metals was conducted using an electrochemical probe system (HSV-100, Hokuto Denko) with gold probes as electrodes. The surface morphology of the films was observed by field emission scanning electron microscopy (FESEM, JEOL, JSM-7001FA).

3. Results and Discussion

Typical SEM image of the poly (amic acid) with trench structure (L/S = 50 μm) is shown in Fig. 2a. It was observed that the regular trench structure of silicon template was successfully transferred on the surface of poly (amic acid) film. The silver thin film can be deposited on poly (amic acid) by applying voltage, through the reduction of silver ions at cathode surface and exchange reaction of doped ions bound to carboxylate anions in the precursor film. Oxidation of water to generate oxygen gas occurred at anode surface. Optical microscope images of the films after electrochemical reaction are shown in Fig. 2b and c. The silver thin film “patterns” was deposited after electrochemical reaction at 2.0 V for 1min. The pattern formation indicates that the reduction of silver ions occurs only at convex portion of trench structure of poly (amic acid) film (contact point with cathode ITO surface). Since the process presented here proceeds in contact area-specific manner, i.e., line width depends only on the initial surface structure of the precursors, narrower line patterns (L/S = 10 μm) can be readily fabricated by using silicon template with different trench structure (Fig. 2c).

Fig. 3 shows the effect of the reaction time on the morphology of the deposited silver thin films. The grain size of the film is found to increase slightly as the deposition time increases (Fig. 3a, b), which can be caused by continuous reduction and diffusion of silver ions initially distributed in whole of the PAA film. Dense, conductive silver thin films with thickness of ca. 70 nm can be obtained after deposition for 3 min (Fig. 3c).

The present process can be extended to fabricate copper patterns. Only the difference is that the amount of divalent copper ions doped into the poly (amic acid) is half of monovalent silver ions. After electrochemical deposition for copper ion-doped precursor at 8.0 V for 1 min (higher voltage is needed for copper deposition due to lower concentration of divalent copper ions), the copper patterns can also be fabricated on poly (amic acid) as shown in Fig. 2d.

The deposited silver and copper thin films were remained on the precursor surface (not on ITO surface), indicating strong adhesion of the metals with underlying precursor substrate through nanoscale granular structure at the interface. Importantly, subsequent acid treatment using HCl followed by heat treatment for the precursors with deposited metals caused extraction of remaining silver ions from PAA films and dehydration of the poly (amic acid) to form imide rings, respectively, providing polyimide films with highly adhesive metal circuit patterns.

4. Conclusion

The silver and copper patterns were successfully fabricated on poly (amic acid) with trench structure by combining imprint and electrochemical lithography. The features relies only on those of the initial surface structure of precursors, which can be simply controlled by initial choice of the template for imprinting process. This process is simple, environmentally friendly, and fully additive-based methodology for direct fabrication of metal circuit patterns on polyimide-based resins.

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