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New Strategy for Electrochemical Micropatterning of Nafion Film in Sulfuric Acid Solution

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ABSTRACT

A new strategy of confined etchant layer technique (CELT) for the micropatterning of Nafion film was described and tested. The local decomposition of polymer is realized by using an electrochemically combined chemical system to ignite and scavenge the radical reaction of polymer. For micropatterning, a copper mold is employed as the working electrode in a three-electrode cell that also contains a reference electrode and a counter electrode. Whereas the mold electrode is naturally placed on a Nafion film/glassy carbon (GC) sheet workpiece, the self-weight of the mold electrode and the soft feature of Nafion film result in a tight contact between the electrode and film. When the mold is electrochemically oxidized, the GC sheet works as a bipolar electrode in this electrochemical system. The GC sheet surface close to the mold acts as the cathode of a thin-layer electrolytic cell that has contained the mold anode and Nafion electrolyte. The rest of GC surface as the anode of bipolar electrode forms another cell with the counter electrode in bulk solution. In the thin-layer electrolytic cell, the oxidation dissolution and the reduction deposition of metal copper simultaneously occur. Specially, the deposited metal can be re-oxidized after growing up to contact with the mold anode, so as to result in a redox cycle of metal copper within Nafion film. When an additional copper sheet contacts with the GC sheet to undertake the anode function of GC bipolar electrode, the redox cycle can be conveniently established at the low potential and cause the large current. Importantly, this redox cycle enables to maintain the decomposition of Nafion via radical intermediates, but the radical reactions can be controllably interrupted by using 4-amino-2,2,6,6-tetramethyl-l-piperidinyloxy (TEMPO) as a radical scavenger. For Nafion film containing TEMPO, the decomposition of polymer is confined within a very thin layer around the mold surface. This novel method allows us to etch micropatterns with no need of any distance-adjustment equipment, which plays a key role in current micropatterning technologies such as scanning electrochemical microscope.

1. Introduction

The micropatterning of functional polymers has increasing applications in the fields of biosensor, tissue engineering, microfluid and semiconductor processing.[1–6] Nevertheless, the soft feature of polymers makes it difficult to create well-defined structures on their surfaces in the material removal way. Hitherto, the micropatterning of polymers mainly counts on force lithography, energy-beam (i.e. photons, electrons or ions) lithography and oxidative probe lithography.[7–23] These techniques generally suffer from high cost, prolonged time, or need for multiple processing steps. Therefore, new strategies for the simple, affordable and high-efficient micropatterning of polymers are highly desired.

Versatile electrochemistry is a well-known prolific source for new processing methods.[24–26] Either direct or indirect electrochemistry can be employed to achieve corrosion. The direct method requires the use of a workpiece as the electrochemical electrode. For example, by applying a proper bias between the workpiece and the tip of scanning tunneling microscope (STM) or atomic force microscope (AFM), oxidative probe lithography can locally oxidize the materials below the tip.[13–15] Nevertheless, the processable objects are restricted to conducting substrates and ultrathin organic layers prepared by Langmuir-Blodgett or self-assembled means.[27–29] Indirect method allows the workpiece not to connect into an electrochemical system, e.g., scanning electrochemical microscope (SECM), so as to enable the processing of all kinds of materials including the thick fluoropolymers film.

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[30–34] The etchant electrochemically generated at the tip of the ultramicroelectrode can chemically corrode the workpiece, when the ultramicroelectrode of SECM approaches to the workpiece by using the high precision distance-adjustment equipment. However, the fabrication by scanning the ultramicroelectrode point by point is the essential to cause low processing efficiency. In addition, the etchant diffusion may significantly decrease the extent of local etching.

To improve the indirect electrochemistry method, Tian et al. originally proposed a confined etchant layer technique (CELT).[35] The major features of CELT are to compact the etchant diffusion layer and to replace the ultramicroelectrode with a mold electrode. The processing procedure and principle are described in Scheme 1, where electrochemically combined chemical system is presented as a side view. The etchant is electrochemically generated from its precursor at the mold electrode surface. Normally, the diffusion of etchant into bulk solution results in a thick etchant layer. When an additional scavenger in the solution rapidly destroys the diffusing etchant back to its precursor, the etchant is confined within a very thin layer around the mold surface. The profile of CEL retains the fine structure of mold surface. By using the high precision distance-adjustment equipment, the mold approaches to the workpiece until CEL contacts and starts to etch the workpiece surface via the feedback model. As the corrosion going on, the workpiece surface gradually separates itself from CEL, resulting in a self-limiting corrosion process. To maintain the corrosion, the mold must reapproach to the workpiece. This approaching and etching procedure may be repeated for several times in the whole fabrication process. Finally, a complementary pattern with the profile of mold is etched on the workpiece surface. The CEL thickness decides the etching precision.

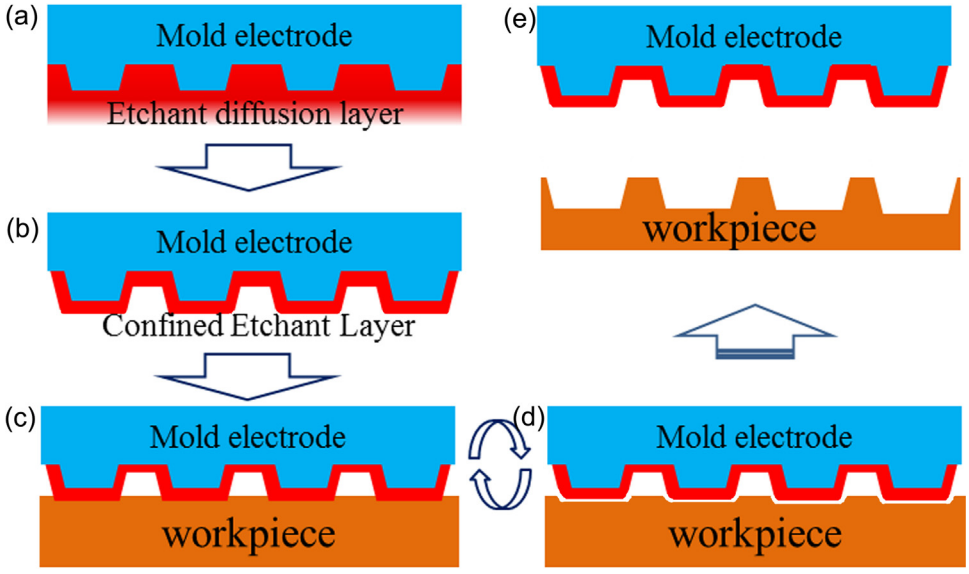
During the past decades, the CELT has been further developed and applied in our lab.[36–40] Unfortunately, the micropatterning of functional polymers, such as Nafion film, has not yet been achieved. The controllable cleavage of carbon-carbon chains of polymers remains a major challenge. Previous literatures reported that hydroxyl radical generated from Fenton reaction could cause the decomposition of polymers. [41–43] However, we have never managed to find a suitable scavenger for Fenton reaction, because hydrogen peroxide is a strong oxidant used as the precursor of Fenton regent.

Most recently, it was reported that copper catalysts are capable of dominating the reversible-deactivation equilibrium of radical polymerization.[44] Besides, copper electrode has been found to enable the electrochemical oxidation of alcohol, carbohydrates and aliphatic diols via radical intermediates.[45] These radical reactions intrigue us to design a new CELT strategy for the micropatterning of Nafion film by using a copper mold electrode. The key features of this new CELT strategy include: 1) utilizing the self-weight of the mold electrode and the soft feature of Nafion film to achieve and retain the natural contact between the electrode and film without any help of distance-adjustment equipment; 2) utilizing the redox cycle of metal copper with Nafion film to ignite the decomposition reaction of Nafion via radical intermediates; 3) employing radical scavenger in Nafion film to confine the decomposition of polymer within a very thin layer around the mold surface. The fabrication following this new strategy should be simpler than the traditional one described in Scheme 1. In this article, the processing procedure and principle were preliminarily explored.

2. Experimental Section

For the preparation of the copper electrode, copper wire (99.995%, 500 μm-diameter) was mounted into a Teflon sheath (2 mm-diameter) filled with epoxy resin (SPI-Pon-812, SPI). After being solidified at 60 °C under vacuum for 48 h, the epoxy-sealed side was polished to expose the metal disc.

For the preparation of the mold electrode, copper sheet (99.995%, 10 μm-thickness) was cut into a 2.5 cm strip and then was coiled on a cylinder. Epoxy resin was pipetted onto the metal reel circulated by a Teflon ring (2 mm-diameter) and was allowed to be solidified. After being taken off from the Teflon ring, both sides of the metal reel/epoxy disk were polished with fine paper to expose all the end planes of the metal reel. One side of the disk was deposited with gold and then attached to the end of a steel cylinder by conductive silver glue.



Scheme 1. The schematic illustration of CELT for micropatterning of workpiece. a) the etchant is electrochemically generated at the mold electrode surface; b) a very thin CEL is formed around the mold surface due to the presence of scavenger in the solution; c) CEL contacts and starts to chemically etch the workpiece surface; d) the material removal leads to a self-limiting corrosion process; e) a negative copy of mold surface is fabricated by repeating the approaching and etching procedure.