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Spontaneous dewetting-induced residue-free patterning at room temperature

Se-Jin Choi *, Dongha Tahk, Hyunsik Yoon

School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, South Korea

A R T I C L E I N F O

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A lithographic patterning method is presented that is based on dewetting induced by sequential molding under an applied pressure. Because of spontaneous dewetting taking place, the window to be opened is free from any residue and the surface exposure is instantaneously assured. This residue-free patterning can be accomplished without any heating process and surface treatment, irrespective of pattern duty ratio. The residue-free patterning is made possible with the use of a rigiflex mold and a roller that is used to bring about pressure-induced thinning leading to spontaneous dewetting. A necessary condition for the method is that the spreading coefficient of spin-coated liquid be negative. The exposed surface can be utilized as a sacrificial layer for etching of underlying layer and/or thin film deposition in a fabrication of electronic and biological devices.

1. Introduction

Over the past decade, a number of unconventional lithographic techniques have extensively been developed as alternatives to the conventional photolithography for patterning micro- and nanoscale features. These include hard template-based nanoimprint lithography [1,2], step and flash imprint lithography [3] in which a quartz mold and photocurable polymer are used, and poly(dimethylsiloxane) (PDMS)-based soft lithography (microcontact printing [4,5], microtransfer molding [6], replica molding [7], micromolding in capillary (MIMIC) [8,9], and solvent-assisted micromolding [10]). Although these techniques provide a simple and useful way of fabricating micro- and nano-structures, they leave behind a residual layer after patterning that needs to be removed later. Fabrication of electronic and biological devices requires the exposure of substrate surface at the windows to be opened. Exceptions are microcontact printing and MIMIC. However, these techniques are not suitable for device fabrication because of poor fidelity of the pattern due to ink smearing and too thin a layer for subsequent etching in the case of microcontact printing and because of applicability of MIMIC only to interconnected patterns. There are other unconventional methods such as capillary force lithography [11] and soft molding [12] in which the surface exposure is possible. In many cases, however, the patterned film is too thin to be useful for subsequent etching.

Dewetting, in particular spontaneous dewetting [13–15], has recently been utilized for residue-free patterning [16,17]. These methods accompany a thermal cycle (heating followed by cooling) since the temperature has to be raised above the glass transition temperature of the polymer being patterned. Even with these techniques, it is difficult, if not impossible, to get the window area on the substrate exposed when the duty ratio is low. The duty ratio is the ratio of line width to the space between lines in line and space pattern. When this ratio is low, the material on a large area has to be all collected into a small area in the course of patterning. Because of the difficulty in low-duty-ratio patterning, low-duty-ratio patterning using selective dewetting behavior on a pre-patterned heterogeneous surface [18] and a two-step dewetting method for large-scale patterning [19] have been proposed for fabrication of a etch mask. However, they could not be applicable without thermal treatment to induce dewetting. On the contrary, some works for residue-free patterning at room temperature have been exploited using a liquid state precursor. Even though soft molding and dewetting of UV-curable poly(ethylene glycol) using poly(dimethylsiloxane) (PDMS) stamp [20] have provided some potentially useful applications including a lithographic resist in fabricating electronic devices and a resistant layer for preventing nonspecific adsorption of proteins or cells, the results were very limited to simple geometrical structure. On the other hand, the discontinuous dewetting of the liquid filament of a sol–gel solution between two surfaces [21] has been utilized to fill nanochannels with no residue on the rest of the top surface. In the nanofilling method, however, not only a substrate with patterned channels should be prepared using some patterning routes but also the shape of preformed pattern should be controlled properly for successful discontinuous dewetting. An ultimate in the residue-free patterning is one in which the patterning can be accomplished in one step at room temperature regardless of the duty ratio. More recently, the microimprint lithography using a soft mold has

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* Corresponding author. Fax: +82 31 732 8788.
E-mail address: saltchoi@snu.ac.kr (S.-J. Choi).

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demonstrated the feasibility for a zero residual layer in one step without any heating process, but requires pretreatment steps on both surfaces of substrate and mold as well as too long period (~2 h) for making zero residual-layer patterns [22].

In this study, we present a method for residue-free patterning that can be quickly accomplished at room temperature without any heat treatment irrespective of the duty ratio. The characteristics of ultra-violet (UV) curable material and mold material are the essential features of the method. The UV-curable precursor liquid has a viscosity low enough for high fluidic mobility and provides a spreading coefficient that is negative. The transparent mold is rigid and yet flexible, i.e., a rigiflex mold made of poly(urethane acrylate) [23,24]. The flexibility allows for sequential conformal contact of the mold with the underlying layer in the course of the patterning.

2. Materials and methods

2.1. Materials for residue-free patterning

The UV-curable precursor used for patterning in this work is a mixture of photoinitiator and the blend of an acrylate functionalized prepolymer and diluent. 1,4-Butandiol diacrylate was used for the acrylated prepolymer, which was used as received from Sigma–Aldrich Inc. At the same time, low viscous reactive monomers, tetrahydrofurfuryl acrylate and hydroxylethyl acrylate, were used as a reactive diluent to reduce the viscosity. Additionally, Darocur 1173 (2-hydro-2-methyl-1-phenyl-1-propane, Ciba Specialty Chemicals, Switzerland) as a photoinitiator was simply blended with the mixture at 5.0 wt.% with respect to the total amount of the blend of the prepolymer and reactive monomer diluent. Then, the mixture was thoroughly mixed. The prepared mixture was stored in a lightless refrigerator. This liquid precursor does not contain any solvent to be dried and can be photocurable at room temperature. The viscosity is less than 10 cPs, which ensures quick thinning of pattern layer due to high fluidity, inducing immediate exposure of thin residual layer in the range of few hundred nanometers as a result of spontaneous dewetting.

2.2. Wet etch of underlying metal layer

To confirm the absence of residual layer, the metal-deposited substrate that residual layer was removed was directly etched using wet etchant, which is the mixed acid consisting of phosphoric acid, nitric acid, and acetic acid (TechnoSemichem Co., Ltd., Korea) in an appropriate ratio. The patterned substrate was dipped in the etchant at 40 °C for 40 s. Prior to wet etch, the samples were annealed in oven at 190 °C for 30 min to enhance the adhesion between the metal substrate and pattern layer.

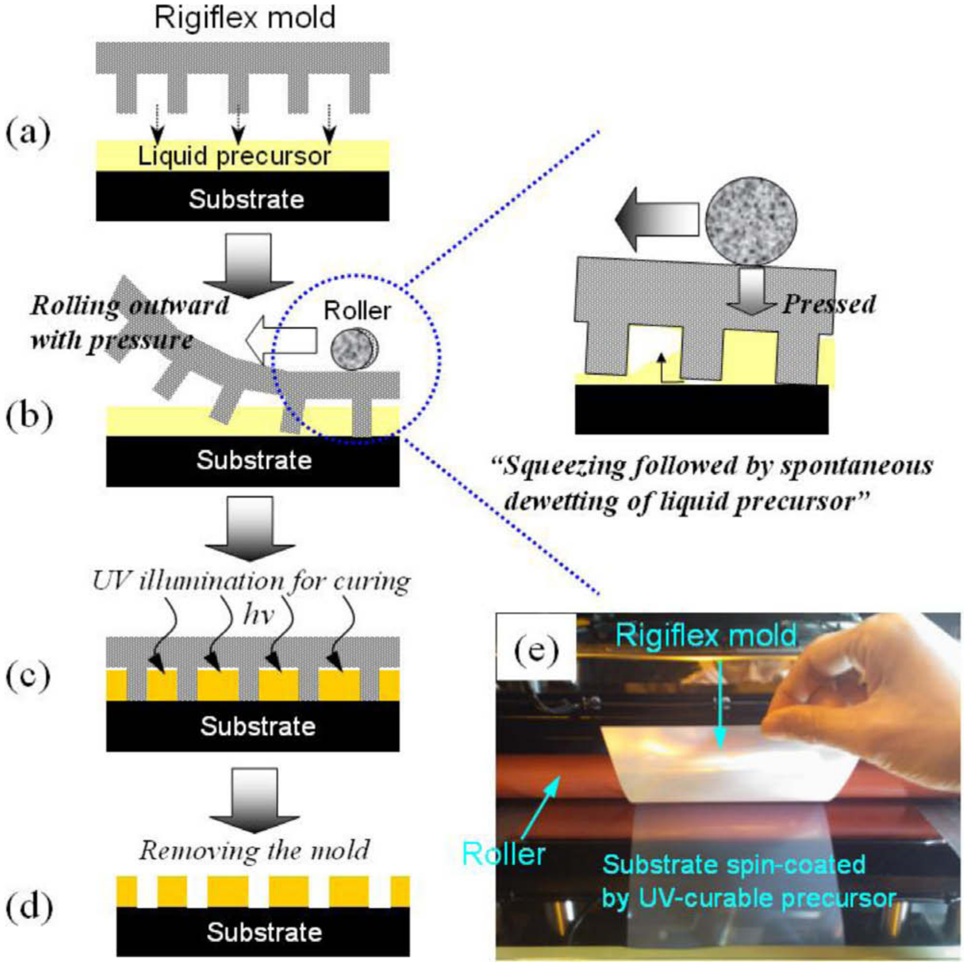

Fig. 1. Schematic illustration of the procedure for residue-free patterning by spontaneous dewetting: (a) A rigiflex mold with desired pattern is put into contact with the layer that is spin-coated on a substrate with a low viscosity liquid prepolymer. (b) A roller is used to press the liquid prepolymer layer against the rigiflex mold surface at room temperature. The right inset shows the sequential nature of the patterning method. (c) Following molding and dewetting, ultra-violet is irradiated through the backside of the transparent mold for curing prepolymer. (d) The mold is removed from cured pattern surface. (e) The captured picture by digital camera in the course of the processing.