Microelectronic Engineering 190 (2018) 38–43

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Research paper

Effect of hydrophilicity of polydimethylsiloxane stamp in capillary force lithography process of thermoplastic polyurethane

Chang Mo Han, Bong-Kee Lee *

School of Mechanical Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, Republic of Korea

ARTICLE INFO

Article history:
Received 13 October 2017
Received in revised form 4 December 2017
Accepted 2 January 2018
Available online 04 January 2018

Keywords:
Capillary force lithography
Hydrophilic stamp
Polydimethylsiloxane
Capillary filling
Polyurethane

ABSTRACT

In this study, effects of hydrophilicity of polydimethylsiloxane (PDMS) stamps and processing parameters in a capillary force lithography (CFL) process were investigated to achieve an improved replication quality. CFL is considered as a simple and versatile technique to replicate micro/nano-features precisely. As a capillary force between a polymer melt and stamp is a major factor for a melt filling, to increase a surface energy of the stamp can help to produce the enhanced filling into micro/nano-scale cavities. In this regard, the inherent hydrophobic nature of PDMS, which is commonly used as a stamp material in CFL, was efficiently turned into hydrophilic using a surfactant in this study. The CFL experiments using hydrophobic and hydrophilic stamps having the micro-line cavities were carried out to imprint the micro-line patterns onto the compression-molded thermoplastic polyurethane (TPU) film. From the characterization of the replicated patterns, it was found that the hydrophilic stamp could exhibit the improved replication quality of 16.78% compared to the typical hydrophobic stamp. In addition, temperature was found to be the most influential among the processing parameters investigated in this study.

1. Introduction

Nowadays, various micro/nano-fabrication processes are employed for a production of functional micro- and nano-scale structures and parts. Depending on the final structure and material, there are many available approaches from the sophisticated lithographic techniques (e.g., electron beam lithography [1], focused ion beam lithography [2], and nano-imprint lithography [3]) to advanced three-dimensional free-form fabrication processes [4]. Because of the outstanding recent advances in the micro/nano-scale fabrication technology, a mass-production of more complex micro/nano-features as well as a development of functional application systems have been efficiently realized. However, it is still required to develop the fundamental fabrication technology in micro- and nano-scale because a precise and rapid manufacturing of micro/nano-features is an essential step to produce the advanced micro/nano-engineered systems.

Capillary force lithography (CFL) is a simple and versatile technique which can be employed to precisely replicate micro/nano-features [5]. After the stamp or mold having the micro/nano-scale cavity is placed on the polymer film, temperature is increased up to the glass transition temperature of the used polymer film. While a viscous force of the polymer material is decreased due to the temperature increase, a capillary force between the polymer and stamp wall becomes more effective. The capillary force is a main driving force promoting a filling of polymer material into the micro- or nano-scale cavity in the stamp, thereby forming precise polymer patterns on a substrate. Once the stamp or mold having the micro/nano-scale cavity on its surface is carefully prepared, a simple replication of precise polymer micro/nano-features can be achieved without any complicated setup and process. In this regard, CFL has been employed in various application fields, including superhydrophobic surface [6], dry adhesive structure [6], biomaterial structures for tissue engineering [7], organic semiconductors [8], and so on.

Polydimethylsiloxane (PDMS) is one of the typical thermally curable elastomers showing a highly elastic property. Due to its excellent properties including strong chemical resistance, simple processing, and optical transparency, PDMS has been widely used in several micro/nano-engineering areas [9]. For instance, most of lab-scale microfluidic systems are usually manufactured using a couple of PDMS plates bonded together. In addition to the microfluidic application, there have been also many efforts to utilize the PDMS stamp or mold in the polymer replication processes [10–12]. As an inherent hydrophobic nature and flexibility of PDMS enables an easy and safe release of the polymer structures from the stamp, the PDMS stamp was considered to exhibit a good performance in the demolding step [13].

While the hydrophobicity of the PDMS stamp helps to obtain the better demolding, it was also reported that the hydrophobic surface can reduce the filling of the polymer melt. Therefore, various techniques to convert the hydrophobic surface of the native PDMS to hydrophilic

* Corresponding author.
E-mail address: b.lee@chonnam.ac.kr (B.-K. Lee).

https://doi.org/10.1016/j.mee.2018.01.001
0167-9317/

have been proposed and investigated. As the representative examples, the temporary modification with an oxygen plasma treatment and the permanent treatment using a thin chemical layer deposition [13–15] were reported. In the case of CFL, even though PDMS is commonly selected as the stamp material, there have been little efforts to investigate the effect of hydrophobic or hydrophilic surface on the replication quality in detail.

In this regard, the effect of hydrophilicity of PDMS stamp and processing conditions during the CFL process were investigated in this study. The inherent hydrophobic nature of the PDMS surface could be efficiently turned into hydrophilic using the surfactant. Both hydrophobic and hydrophilic stamps were prepared to have the same micro-line cavities, which were filled with a thermoplastic polyurethane (TPU) melt by CFL process. The CFL process was carried out based on the design of experiments (DOE) using the orthogonal array. By analyzing the measured results of the imprinted TPU micro-line patterns, the effect of several relevant factors was extensively investigated.

2. Experimental

2.1. Fabrication of hydrophilic polydimethylsiloxane stamp

In this study, the hydrophilic stamp was fabricated simply by adding the surfactant into the conventional PDMS mixture [16]. The included surfactant can efficiently increase the surface energy of PDMS, thereby reducing the apparent water contact angle. In this manner, the PDMS stamp with the hydrophilic surface can be obtained only by slightly altering the conventional PDMS casting process which produces the hydrophobic surface.

As the first step, the SU-8 (SU-8 2007, MicroChem) micro-line patterns were formed as the master structure of the subsequent PDMS casting. The conventional UV-photolithography was used for a fabrication of the micro-line patterns on the 4-in. Si wafer. Each micro-line pattern was designed to have a width of 5 μm, pitch of 45 μm, and height of 10 μm. For the PDMS casting process, two types of the PDMS mixture were prepared. The typical mixture of PDMS monomer and curing agent (Sylgard 184A and B, Dow Corning) in a 10:1 weight ratio was prepared for the hydrophobic stamp. For the hydrophilic stamp, 1 wt% of Silwet L-77 (Momentive) was added into the typical PDMS mixture as the surfactant. The mixtures were poured onto the SU-8 master of the micro-line patterns. After degassing and curing at 60 °C for 4 h, the cured PDMS stamps were carefully peeled off from the SU-8 master. As the SU-8 master had the protruding micro-line patterns, the replicated PDMS stamps were fabricated to have the micro-line cavities with the same dimensions.

2.2. Compression molding of thermoplastic polyurethane films

TPU (K-385A, Kolon Industries) was selected as the CFL resist in the present study. Because it has a moderate level of the glass transition temperature around 105 °C, the typical polymer processing technologies of thermoplastics can be directly used to prepare the thin TPU films. In addition, the selected TPU has a quite high elongation (~630%) and low stiffness (Young's modulus of 20 MPa), which is advantageous to achieve an easy demolding without any defects in the precisely replicated micro-features. Furthermore, its good optical property make it possible to be used in the microfluidic and optical applications. In this regard, the current CFL process was carried out to imprint micro-line patterns onto the TPU film.

For the CFL experiment, the thin circular films of TPU were fabricated using a compression molding of TPU pellets. From the feasibility experiment, the processing conditions for the compression molding of TPU films were determined. After placing the weighed TPU pellets between two flat platens of the compression molding machine, temperature was increased up to 160 °C. Then, compressive force of 1275 N was applied for 3 min. When temperature was decreased down to 50 °C by cooling, the applied force was removed and the produced TPU film was separated from the platens. In this manner, the thin circular TPU films with 86 μm in thickness and 23.4 mm in diameter could be prepared. It might be noted that as the compression-molded TPU films were fabricated to have the flat surface, the micro-features could be imprinted on the film's surface during the subsequent CFL experiment.

2.3. Capillary force lithography process

In this study, the CFL experiments using two types of PDMS stamps were carried out to investigate the effect of hydrophilicity of the PDMS stamp. While a thermoplastic CFL resist has the glassy state at the room temperature, it becomes rubbery with increasing temperature. When temperature is increased further, viscosity of the thermoplastic material is rapidly reduced, thereby resulting in the melt state. In addition, if the characteristic dimension is small enough not to ignore the surface forces, the capillary force between the thermoplastic melt and surrounding stamp wall becomes dominant over the viscous force. In this manner, the filling of micro- and nano-scale cavities with the melt is obtained in the case of the typical CFL process.

To systematically investigate the effects of the relevant processing parameters and hydrophilicity of the PDMS stamp, the DOE technique based on the orthogonal array was employed. Three processing parameters of temperature (T), time (t), and additional compressive force (f) were chosen as the major factors. Each parameter was designed to have three different levels as listed in Table 1 from the feasibility experiment. Because three parameters with three levels were considered together with one additional parameter of hydrophilicity, the first four columns of $L_{18}(2^1 \times 3^7)$ orthogonal array (Table 2) were selected to determine the experimental sets considering the complicated effects from the detailed processing conditions. It should be mentioned that the effect of each parameter could be efficiently analyzed with a minimum number of experiments because of the nature of the orthogonal array [17,18]. For example, the filled height under the temperature of 160 °C using the hydrophilic stamp could be found by taking a mean value of three results from the experimental sets #1, #2, and #3.

For the CFL process, the compression-molded thin TPU film was placed on the stainless steel plate. On top of the TPU film, the PDMS stamp was carefully laid. When the additional compressive force (f) was applied, the precision balance with a defined mass was also laid on the PDMS stamp. The whole part was put inside the convective oven whose temperature was controlled to be the setting temperature (T). After the setting time (t), the temperature was reduced down to room temperature. Then, the PDMS stamp was peeled off from the molded TPU film where the micro-line patterns were imprinted from the used PDMS stamp.

3. Results and discussion

3.1. Hydrophilic stamp

Fig. 1 shows the hydrophilic PDMS stamp fabricated in the present study. Because the SU-8 master of the micro-line patterns was used in the PDMS casting, the PDMS stamp was produced to have the micro-line cavities. After peeling off the cured PDMS structure, the small piece of 10 × 10 mm^2 was cut from the entire structure for the convenient CFL process (Fig. 1(a)). Fig. 1(b) shows the microscopic view of

Table 1
Processing parameters and their conditions used in the present CFL process.

Parameters	Level		
	1	2	3
T, Temperature (°C)	160	165	170
t, Time (min.)	30	60	90
f, Additional compressive force (g-f)	0	5	10