Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Microlens fabrication by replica molding of frozen laser-printed droplets

Salvatore Surdo, Alberto Diaspro, Martí Duocastella *

Nanophysics Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

ARTICLE INFO

Article history:
Received 30 June 2016
Received in revised form 9 November 2016
Accepted 10 November 2016
Available online xxx

Keywords:
Microlens fabrication
Laser-induced forward transfer
Soft-lithography
Replica molding

ABSTRACT

In this work, we synergistically combine laser-induced forward transfer (LIFT) and replica molding for the fabrication of microlenses with control of their geometry and size independent of the material or substrate used. Our approach is based on a multistep process in which liquid microdroplets of an aqueous solution are first printed on a substrate by LIFT. Following a freezing step, the microdroplets are used as a master to fabricate a polydimethylsiloxane (PDMS) mold. A subsequent replica molding step enables the creation of microlenses and microlens arrays on arbitrary selected substrates and by using different curable polymers. Thus, our method combines the rapid fabrication capabilities of LIFT and the perfectively smooth surface quality of the generated microdroplets, with the advantages of replica molding in terms of parallelization and materials flexibility. We demonstrate our strategy by generating microlenses of different photocurable polymers and by characterizing their optical and morphological properties.

1. Introduction

Integration of micro-optical elements into traditional systems is emerging as an effective and sustainable approach for the realization of devices with enhanced performance and extended functionalities [1]. Successful examples include the use of microlens arrays for increasing light extraction efficiency in organic-light emitting diodes and solar cells [2,3], or the use of microlenses for enhancing both imaging throughput and sensitivity of cameras and optical sensors [4]. Unfortunately, the rapid development in fields such as energy harvesting or camera manufacturing has imposed additional requirements in the fabrication of micro-optical components that cannot be fulfilled with existing technologies. Indeed, besides ensuring high optical quality, the fabrication of microlenses on targeted positions over different substrates, the selection of the geometry of the microlens arrays, or the reduction in cost and processing times, have become issues of utmost importance that traditional fabrication strategies, such as photolithography with thermal-reflow, fail to accommodate. For instance, widely used lithographic techniques are restricted to planar surfaces, they strive to integrate common optical materials such as transparent polymers and, more importantly, require masks or molds that are costly and time-consuming to fabricate [5]. Promising alternatives capable to rapidly generate, in a single step, an entire array of micro-optical components over large areas are soft-lithography approaches. These techniques use elastomeric molds for microlenses replication (i.e. replica-molding) or for patterning pre-polymer microdroplets (i.e. micro-contact printing) that are converted into microlenses by exposure to UV [6,7]. Despite proven success of the use of soft-lithography for microlenses or microlens arrays fabrication [7], the preparation of the mold still remains a time-critical step that drastically limits the overall process efficiency [8]. This is particularly problematic when small customized systems are desired, or for rapid prototyping. In fact, the most common method to generate the mold is by casting a liquid curable prepolymer (i.e. polydimethylsiloxane or PDMS) against a master patterned using photolithography.

A different family of non-lithographic processes capable to rapidly generate tailored microlenses or microlens arrays on targeted positions on a substrate are direct-writing technologies (DWTs) [9]. In particular, wet-based DWTs such as ink-jet printing [10] or laser-induced forward transfer (LIFT) [11] can directly deposit microdroplets of different materials onto a substrate according to a user-selectable design without the need of intermediate steps. Surface tension makes the generated liquid microdroplets almost perfectively spherical surfaces, and hence can be directly used as microlenses [12]. By printing photocurable prepolymers, an additional curing step can convert the microdroplets into solid microlenses, making DWTs an extremely versatile tool

* Corresponding author.
E-mail addresses: marti.duocastella@iit.it, duocastella@gmail.com (M. Duocastella).

http://dx.doi.org/10.1016/j.apsusc.2016.11.077
0169-4332/

for the fabrication of micro-optical elements [13,14]. However, the particular focusing properties of the generated microlenses can only be partially controlled by the user. In more detail, even if the radius of curvature of the microlenses and its focal length can be selected by changing the droplet diameter, the effective numerical aperture (NA) is only determined by the contact angle of the droplet with the particular substrate used. By modifying the wetting properties of the printed liquid with the substrate (e.g. adding surfactants), it is possible to change the microlens NA, but this also modifies the optimal printing conditions. In fact, a current drawback of current wet-based DWTs is that for each particular substrate or material used, the optimal printing conditions must be experimentally determined. Ideally, one would like to have a method that maintains the advantages of DWTs while allowing control of the optical properties of the fabricated microlenses over different printed materials and targeted substrates.

In this work, we present a novel approach that combines the advantages of soft-lithographic techniques with those of DWTs while preventing their intrinsic limitations. Our multistep strategy is based on using a wet-based DWT to print droplets of a model aqueous solution on a standard substrate. Notably, we select a solution whose optimal printing conditions are already well-characterized in literature. In a subsequent step, we freeze the liquid microdroplets, and we use them as a master to fabricate a PDMS mold. Once the PDMS mold is ready, we can simply employ replica molding to fabricate the corresponding micro-optical elements on any desired substrate and by using any desired curable polymer. Therefore, our methods allows us to rapidly fabricate molds with high optical quality by exploiting the advantages of DWTs, while maintaining the parallel nature of soft-lithography and its capacity to generate microlenses of different materials, regardless of their specific wettability on the substrate used.

2. Materials and methods

2.1. Laser direct writing system

The experimental direct-write system for printing liquid microdroplets consisted of a 100 kHz Ti:sapphire femtosecond laser (Coherent) emitting 100-fs-long pulses at the operation wavelength of 800 nm. The laser beam was focused onto the sample by a 10X, 0.28 NA long-working distance objective (Mitutoyo M Plan Apo 10X), and the laser energy was adjusted using a rotating $\lambda/2$ waveplate and a polarizing beam splitter. The sample was positioned with respect to the focused laser beam by a computer controlled XYZ translation system (Prior Scientific) with resolutions of 0.01 μm in both X and Y and 0.002 μm in Z. A CCD camera (Thorlabs) was placed coaxially to the laser beam for imaging the sample in situ. The focal plane of the camera was located near to the focal plane of the laser. Thus, CCD images served to estimate the position of the laser beam waist.

2.2. Laser printing

The donor used during LIFT was a thin film of a mixture of water and glycerol with a ratio 1:1 by volume. To improve the uniformity of the donor film, 1 mg of sodium dodecyl sulfate (Sigma) was added to 1 mL of the mixture. This is a solution commonly used in LIFT experiments and whose optimal printing conditions have been studied in depth [15,16]. Blade coating was used to spread the liquid on top of a microscope slide covered with a 100-nm-thick chromium film. The chromium was used as a laser absorbing layer since the liquid solution was transparent to the laser radiation. Before the blade coating step, the chromium film was cleaned with soap and deionized water and dried under a nitrogen flux. No other special treatment was performed during sample preparation. The receiver substrate for LIFT was the flat polystyrene base of a Petri dish (BD Falcon). The donor film was placed on top of the polystyrene surface at a distance of about 70 μm using Kapton tape (Thorlabs) as spacers. The relative position of the laser beam with respect to the donor-polystyrene system was controlled by the XYZ stage during LIFT. After the printing process, the microdroplets were frozen using liquid nitrogen that was carefully poured into the polystyrene substrate.

2.3. PDMS mold fabrication

The mold for the microlenses fabrication was obtained by casting PDMS solution (Sylgard 184, Dow Corning) into the Petri dish that contained the frozen laser-printed microdroplets. The PDMS solution was prepared by mixing curing agent and PDMS prepolymer in a 1:10 weight ratio and degassed in a low vacuum desiccator for 1 h to remove any air bubbles. Once the pattern to be replicated was printed with LIFT, a frozen master was created using liquid nitrogen. After the nitrogen was completely evaporated, the PDMS prepolymer was poured onto the frozen master and cured at 65 °C for 40 min [17]. The cured PDMS was peeled off from the polystyrene substrate and was washed out to eliminate any potential residues of the water and glycerol mixture.

2.4. Morphological and optical characterization

The diameter and shape of the printed droplets, and resulting mold and replica were determined by means of optical microscopy (DM2500 M, Leica). Further characterization of the 3D profiles of both mold and replica was carried out using a confocal microscope (Fluoview 1000, Olympus) equipped with an oil immersion objective lens (UPlanSApo 100×/1.40, Olympus). The microlenses topography was numerically calculated by processing a set of confocal images taken over a range of focal planes.

The optical properties of the fabricated microlenses were evaluated by recording the intensity profile of a 532 nm continuous wave laser after passing through the microlens array. A 60×, 0.9 NA objective and a CMOS camera (Thorlabs) was used to capture the intensity distribution at different axial positions and obtain the point spread function (PSF). In addition, imaging performance of the microlenses was determined by using projection experiments in which the cell phone screen acted as a source and a 40×, 0.75 NA objective was used to collect the corresponding image formed by the microlenses.

2.5. Time-resolved contact angle goniometer

The evolution of the contact angle (θ_i) of a frozen droplet on a polystyrene substrate (when PDMS was poured onto it and underwent thermal curing) was recorded using a homemade contact angle goniometer. The system consisted of a LED light source, a digital camera connected to a PC and a hot-plate to control the temperature during the PDMS curing process. The polystyrene substrate and corresponding droplet were located on top of the hot-plate, which in turn was placed between light source and camera.

3. Results and discussion

A schematic diagram of the microlens fabrication process is shown in Fig. 1. The key point of our approach is the rapid preparation of the elastomeric mold (Fig. 1(a)) that can be later used for the fabrication of microlenses by means of replica molding (Fig. 1(b)). To this end, we used laser-induced forward transfer (LIFT) to print water-glycerol microdroplets onto a polystyrene

Please cite this article in press as: S. Surdo, et al., Microlens fabrication by replica molding of frozen laser-printed droplets, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.11.077