Microelectronic Engineering 110 (2013) 112–118

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

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

High aspect ratio pattern collapse of polymeric UV-nano-imprint molds due to cleaning

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ARTICLE INFO

Article history:
Available online 28 February 2013

Keywords:
Nanoimprint
Stamp fabrication
Soft mold
Sticking
UV-NIL
Working stamp

ABSTRACT

Polymeric molds replicated from a master structure can provide intrinsic anti-sticking behavior and UV-transparency. They can be replicated from various substrates and offer cost efficient replication of multiple working stamps from only one master. They also allow the use of various imprint methods including UV- or thermal-assisted ones. Usually, the polymer material exhibits mechanical and surface-chemical properties which differ from hard mold materials like silicon, silicon dioxide or metals. Due to this, the molds might be deformed or even destroyed during imprint or cleaning. This is pronounced for high aspect ratio patterns, as they occur, if imprint is used as direct pattering method. The affinity to pattern damage of polymeric molds during cleaning is investigated in this paper. Different possible polymeric mold materials are considered. Experimental data is compared to simulation results and shows good agreement. Different exemplary patterns are investigated and a best suitable material is found. It is stable for feature aspect ratios up to 10 for half pitch gratings in the considered range of dimensions.

1. Introduction

Nano-imprint lithography (NIL) is a powerful patterning technique offering nano-meter resolution [1], large area structuring capabilities [2] as well as the intrinsic ability to replicate three-dimensional features [3]. During the last years, many different NIL processes have been proposed. UV-light assisted NIL (UV-NIL) [4] eliminates the thermal load to the system during imprint and enables the efficient synthesis of functional imprint resists [5]. UV-NIL requires either the substrate or the mold to be UV-transparent. As the transparency of the substrate is mostly driven by the application, UV-transparent molds are preferable. Unfortunately, the most commonly used stiff mold material is fused silica which requires elaborate processing. Dry-etch processes of fused silica can only offer limited etch depth and resolution simultaneously. This limits the addressable applications for UV-NIL. The use of polymer molds cast from a master (cf. Fig. 1), sometimes referred to as soft lithography [6], offers many advantages as the used polymers can be UV-transparent, intrinsically anti-sticking and flexible. Therewith, e.g., printing over particles [7] or the replication of features with undercuts [8] become possible. The comparable low Young's modulus of the soft polymer mold yields unwanted feature deformation during imprint. This limits the application of UV-NIL as direct patterning method [9,10], where replicated structures are used as functional elements itself, rather than to serve as mask for subsequent process steps. For direct patterning, the dimensions of the required mold are fully driven by the application and not by the process. Even if suitable process conditions are found to be able to replicate the structures in the mold, pattern deformation can occur during mold cleaning as depicted in Fig. 2. Especially high aspect ratio mold patterns are prone to the so called feature collapse. Mold casting is an elaborate and costly process. Usually special templates and processing is required for polymeric molds to be competitive with rigid stamps with respect to resolution, flatness, residual layer thickness, etc. Simple replication of master structures in a polymer is not sufficient to gain high quality imprints. Therefore, the lifetime of a mold should be as long as possible. Cleaning is an easy way to get rid of uncured resist residuals or particles which otherwise may damage the mold during imprint. Conditions comparable with the ones leading to pattern collapse during resist development [11,12] can evoke persistent feature deformation after cleaning. Besides this effect is used for the generation of special patterns [13], it is an unwanted effect that has to be avoided.

In this paper, different polymer mold materials and there affinity to pattern collapse during mold cleaning are investigated. This also includes materials that are able to replicate structures with a higher aspect ratio than the ones considered in previous publications. Polymer molds were cast from silicon master structures and subsequently cleaned using cleaning agents. The observed pattern collapse has been used to validate finite element

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http://dx.doi.org/10.1016/j.mee.2013.02.065

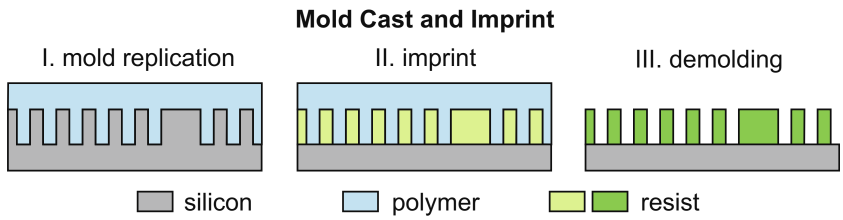

Fig. 1. Process flow of the replication of a master structure into a polymeric mold and a subsequent imprint process.

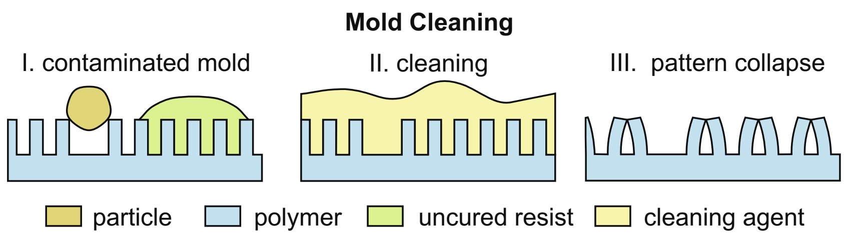

Fig. 2. Cleaning of a polymeric mold containing particles and uncured resist residues using a cleaning agent and a possible resulting feature collapse.

method (FEM) simulations of the collapse process. With the developed model a forecast of the critical structure height can be obtained.

2. Sample preparation

2.1. Master fabrication

Silicon master structures were fabricated by wafer-stepper exposure using an ASML PAS 5500-250C and electron-beam lithography (EBL) using a Vistec SB3050DW. The customized layout basically contained line-space gratings with various pitches from 500 nm to 2000 nm as well as dot-arrays in a quadratic lattice and diameters from 500 nm to 2000 nm with various duty cycles (feature size to pitch). The patterned resist layers were used as etch-mask for a reactive ion etch process [14] to gain different etch depths ranging from 500 nm to 3200 nm in silicon. After resist stripping, a perfluorotrichlorosilane anti-sticking layer (ASL) [15,16] has been applied to the silicon molds by molecular vapor deposition. This lowered the surface energy and ensured easy demolding of the subsequently cast polymeric molds. In principle, this is not necessary for all materials considered in the following, as some show intrinsically low surface energies.

2.2. Polymer mold casting

Polymer molds were cast from the silicon masters with Fluorolink MD700 (MD700) and Fomblin MD40 (MD40) (Solvay Solexis) with 2 wt.% 2-hydroxy-2-methylpropiophenone (Sigma–Aldrich) as photoinitiator as well as OrmoStamp (Microresist Technology (mrt)). Glass slides were used as substrates. APS1 (mrt) was used as adhesion promoter for MD40 and MD700 and OrmoPrime08 (mrt) for OrmoStamp. All materials were manually dispensed on the silicon masters and subsequently brought into contact with the substrates using a customized imprint press. The material was cured using a UV-LED (Nichia NC4U133) under a nitrogen inert atmosphere. A thick residual layer in the order of several 10 μm was present in every polymer mold cast.

2.3. Mold cleaning

Cleaning agents must be able to solve uncured resist residuals and to flush away particles. Further, they should not swell or dissolve the mold material or parts of it. Therefore, all molds in this work were flushed with isopropanol directly after demolding from the silicon master and subsequently dried using a nitrogen stream. During the experiments, also other cleaning agents (acetone,

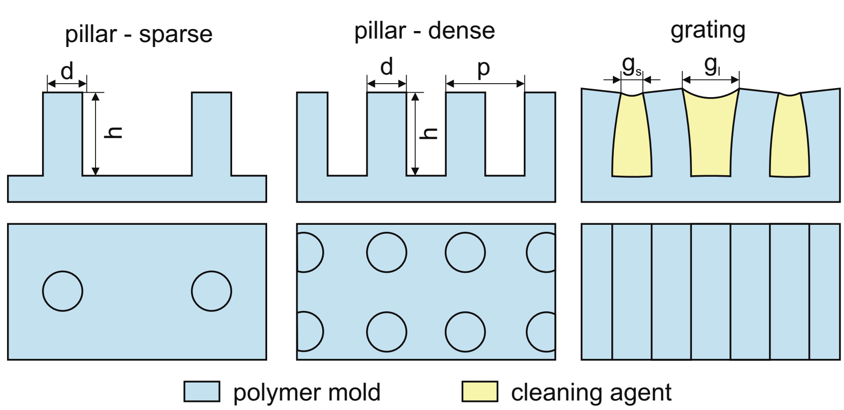

Fig. 3. Sketch of the considered structures: separated pillars, dense pillars and dense gratings with the dimensions used for simulation.