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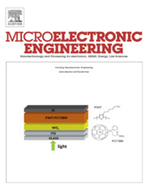

# Residual layer-free Reverse Nanoimprint Lithography on silicon and metal-coated substrates

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ABSTRACT

In this work we demonstrate that Reverse Nanoimprint Lithography is a feasible and flexible lithography technique applicable to the transfer of micro and nano polymer structures with no residual layer over areas of $cm^2$ areas on silicon, metal and non-planar substrates. We used a flexible polydimethylsiloxane stamp with hydrophobic features. We present residual layer-free patterns imprinted using a commercial poly(methylmethacrylate) thermoplastic polymer over silicon, nickel and pre-patterned substrates. Our versatile patterning technology is adaptable to free form nano structuring and has coupling to adhesion technologies.

## 1. Introduction

Nanoimprint lithography (NIL) dates back to 1995 [1] and is currently identified as one of the most promising techniques, due to its potential low-cost, high-resolution and large-area patterning capabilities compared with other lithography techniques. NIL has been used to obtain patterns with sub-10 nm resolution, in thermal [2] and ultraviolet (UV) nanoimprint [3] modes. Furthermore, this technique is compatible with the roll-to-roll process and it is suitable for manufacturing a range of different devices such as optoelectronic [4] or energy devices [5].

Although NIL has been extensively developed, there are still issues that need to be addressed for it to become a mature nano manufacturing technology. One of the challenges is the removal of the residual layer after the imprinting step. Regardless of the type of polymer resists used, a residual layer will always remain between the elevated parts of the stamp and the substrate. Most applications require the elimination of this residual layer via a reactive ion etching (RIE) post processing step [6]. Although RIE is a well-controlled process this additional step increases the overall processing complexity, implies an additional cost and decreases the throughput of the nanoimprint process. In addition, it is possible that the edges of the polymer features become rounded during the RIE process because of the low selectivity of the etching process. Therefore, residual layer-free imprint lithography is indispensable for large-area fabrication.

Various methods have been used to create residual layer-free imprints. Attempts include partial UV-curing of polymer followed by an additional chemical development process [7,8], utilizing flexible molds to directly contact the substrate in order to eliminate residual layer [9,10] and selective filling into the recessed areas of the mold followed by transferring the polymer patterns to a substrate [11,12].

In thermal NIL, imprinting is typically performed at temperatures between 60 and 90 °C above the polymers $T_g$ under pressures as high as 10 MPa [13]. In contrast to thermal NIL reversal imprint lithography (RNIL) is a promising residual layer-free lithography technique which requires low pressures and temperatures. Imprinting temperatures around the polymer $T_g$ are sufficient to achieve a reliable pattern transfer. This technique is used to selectively imprint thin polymer films over flat and/or pre-patterned surfaces [14].

This approach has been followed by different authors. Park et al. tried to remove the residual layer from a surfactant-coated silicon mold. By creating and incompatibility between the surface and the resist, they induced a dewetting process. Heating the substrate above the glass transition temperature of the polymer, the top of the mold could be moved to mold trenches [12]. Kao et al. performed a residue-free RNIL by means of a self-assembly

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monolayer-treated silicon mold [11], inducing a selective filling of the mold by spin coating. All these free residual layer imprints were achieved by means of various process steps, involving chemical treatments. Furthermore, in all cases hard silicon molds were used, which imply higher imprint pressures and limit the possibility of transferring the process to free-form surfaces.

The typical silicon molds used in most of the NIL experiments have several disadvantages, such as cost and brittleness. Furthermore, these kinds of molds make impossible a proper pattern transfer on free-form surfaces, limiting the application scope. Flexible molds, such as those made in polydimethylsiloxane (PDMS) have the advantage of avoiding breakage during direct contact between the mold and substrates and only require low pressure for conformal contact, even in large-area fabrications [10].

Here we show a one-step residual-layer-free patterning method (Fig. 1). By means of the RNIL flexible lithography technique, polymer structures with no residual layer over $\text{cm}^2$ areas on silicon and metallic substrates were achieved as well as on pre-patterned substrates, leading to the possibility of developing 3D structures. We use a flexible PDMS stamp with honey comb like hydrophobic structures as a proof of concept. These honeycomb structures have a spacing of 500 nm and a height of 800 nm. Due to our experimental design configuration (flexible mold), low pressure (1 bar) and temperatures ($T_{imp} \approx T_g$) were sufficient enough to achieve the large area ($\text{cm}^2$) pattern transfer.

This technique, based on the flexibility of the stamp used is transferable to non-planar surfaces and pre-patterned surfaces, given that the stamp can be pressed against a structured surface without break.

The fabrication approach presented in this work is also transferable to any kind of geometry, including those intended for hydrophobic purposes. In these structures the wettability of the resist is a key parameter to take into account, in terms of pattern transfer quality. Furthermore, it is well accepted that wetting phenomena occurring on flat surfaces is quite different from that occurring of patterned ones [15–17].

To study the wettability of a surface, we could take into account two different models, the Cassie–Baxter model [18] and the Wenzel model [19]. The so called Cassie state describes the situation where a droplet partially sits on air pockets whereas the Wenzel state implies a complete wetting of a rough surface, i.e. liquid penetrates into grooves constituting a relief. Therefore, for our experimental approach, a wetting transition towards a Wenzel state is needed in order to assure a complete and uniform distribution of the resist along the flexible stamp. Wetting transitions on rough surfaces have been studied in detail by Bormashenko [20,21] and constitute an interesting topic regarding wetting behavior and tailoring of surface properties through external stimuli [22]. In particular, we have chosen mechanical vibrations as the external source of the required energy to overcome the energetic barrier that separates equilibrium wetting states, from the Cassie towards the Wenzel state.

As an example of this approach, we used the negative polarity of the honey comb like structures, due to the fact that the cavities to be filled have a width of 500 nm.

## 2. Experimental procedure

### 2.1. PDMS replica fabrication

A honeycomb structure was used as mold. Honeycomb designs with 800 nm feature height and 500 nm trench separation were used. Firstly the patterns were defined on a silicon wafer by electron-beam lithography followed by a reactive ion etching step to create the full Si master mold. The Si mold was treated with a fluorinated anti-adhesion layer in order to alter the surface hydrophobicity for easy mold releasing. The coating step was performed by immersing wafers in a low concentration of Optool DSX solution (1‰ wt into perfluorohexane) during 1 min. Then, the wafer was placed in a water environment at 65 °C for 1 h. Finally, the wafer was rinsed in perfluorohexane during 10 min.

The PDMS mold was fabricated by casting the PDMS prepolymer against the relief structure of the silicon master mold. We used the PDMS precursor with a mixing ratio of 5:1 (precursor:curing agent) and it cured for 12 h at 60 °C. We optimized the thickness of the PDMS molds to be 3 mm in order to avoid pattern deformation due to the stretching of the mold [23]. The cured PDMS mold was peeled off manually from the silicon stamp.

### 2.2. Reverse nanoimprint process

The polymer used in this work was poly(methylmethacrylate) (PMMA) with an average molecular weight (MW) of 75,000. In case of a mold with nm features, the thickness of the deposited film is a strong function of the concentration of the solution used for spin

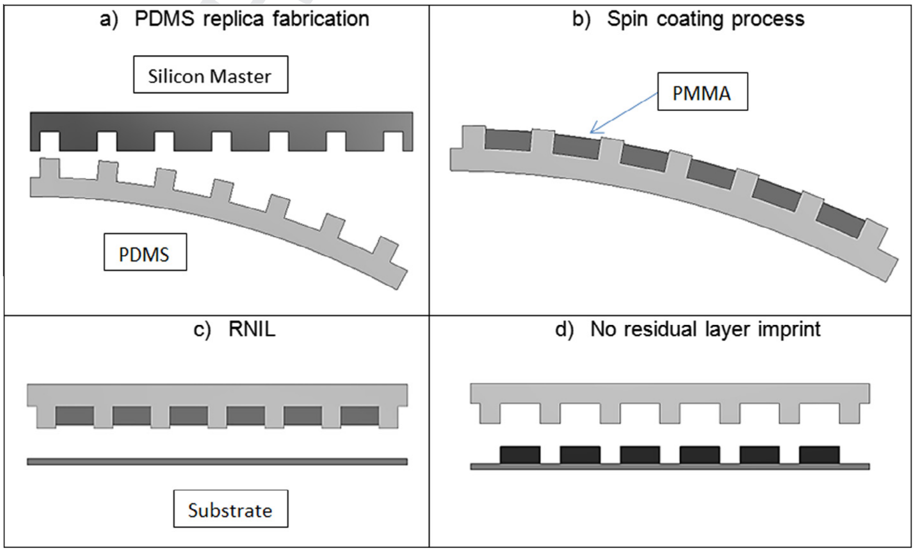

**Fig. 1.** Schematic illustration of the residual-layer-free reversal NIL process.