Study of the transfer of a biosourced resin by thermal nanoimprinting

Paule Durin[1,2], Céline Chevalier[1*], Aziz Benamrouche[1], Radoslaw Mazurczyk[1], Yann Chevolot[1], Didier Léonard[2], Jean-Louis Leclercq[1]
[1]Univ. Lyon, CNRS, INSA Lyon, Ecole Centrale de Lyon, Univ. Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, F-69134 Ecully, France
[2]Univ. Lyon, CNRS, Univ. Claude Bernard Lyon 1, Institut des Sciences Analytiques, UMR 5280, F-69100 Villeurbanne, France

E-mail: celine.chevalier@insa-lyon.fr

Today, lithography raises issues of health and environmental impact. Indeed, the chemicals used to manufacture the resin, additives, chemical synthesis, solvents and developers are mainly petroleum-based, and some of them are hazardous and toxic. To develop a more eco-responsible technology, we propose to use films based on a biosourced polymer, chitosan. Derived from chitin, the second most abundant biosourced polymer on earth, it is water-soluble, biodegradable and non-toxic. Chitosan is highly attractive thanks to its solubility in weakly acidic aqueous media, its film-forming properties and its resistance to etching. For some years now, chitosan films have been used in our group as lithographic resins for UV, DUV and e-beam [1-3]. In addition, it has been demonstrated that chitosan can be used in processes ranging from lithography to plasma etch transfer of sub-micron patterns in cm² silicon up to the scale of a 300 mm industrial pilot line [4].
In order to increase the ability to use such a biobased resin, we have extended its application to conventional one-step nanoimprint lithography without chemical modification of the chitosan or resin formulation. The nanoimprint lithography equipment is a step-and-repeat SET NPS300 - Nano-Patterning Stepper.
Chitosan solutions were spun to produce thin films of around 250 nm on SiO2/Si substrates and cured on a hot plate at 150°C for 5 minutes. Initial tests were carried out with 1D lines 300-400 nm high, 2.5 µm wide and 5 µm apart. Printing was carried out under a pressure of 400 bar (4000N) for 30 minutes, with a 20-minute stop at 150°C. After removal of the Si buffer, we noted good printing homogeneity, but not throughout the resin thickness. AFM observations revealed the presence of raised resin flanks (friction/bonding to the pad walls on removal). To compensate for these effects, the cooling conditions were changed, largely eliminating the bulges observed on removal of a pad with a 2D network of studs - 200 nm in height, 500 nm in diameter and a period of around 1 µm (figure 1). In addition, the applied pressure remained at 400 bar (2600N), and the temperature was raised to 180°C while maintaining the pad and sample at this temperature, enabling printing across the entire film thickness. Moulding/demoulding conditions and residual at the bottom of the hole are very good and can still be optimized.

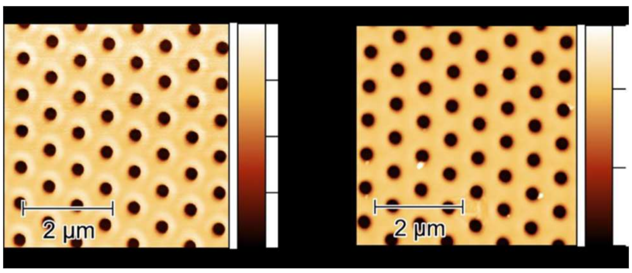

***Figure 1** AFM images (5*5 µm²) of the chitosan resin after printing at the edge (left) and center (right) of the sample.*

These patterns are then transferred by plasma etching into a 300 nm thick thermal silica layer on a Si <100> substrate. The nature of the polymer makes it possible to apply a pre-stage of residual removal at the bottom of the hole by O2 plasma lasting just a few seconds, while preserving the integrity of the patterns defined by nanoimprinting (figure 2).

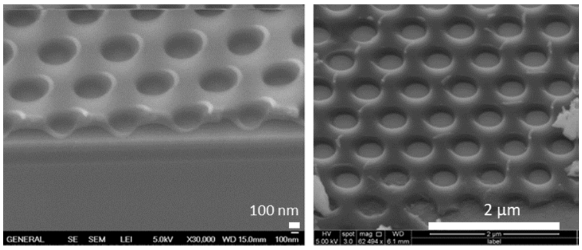

Figure 2 *Scanning electron microscopy images of chitosan films after printing (left) and after the O2 plasma step (right).*

A CHF3 plasma is then applied to faithfully transfer the network of sub-micron holes into the silica, followed by complete removal of the chitosan film by a final O2 plasma.

These initial results clearly demonstrate the ability to use biobased resin films without chemical additives in thermal nanoimprint replication techniques under relatively mild conditions. Their excellent properties under etching plasmas enable them to be used in micro-nanofabrication of devices.

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