# Highly Nonlinear Behavior of UV-curable Photopolymer under Elastomer-templated Low-Pressure Nanoimprinting

Myung Gi Ji<sup>a</sup>, Rabiul Islam Sikder<sup>a</sup>, and Jaeyoun Kim<sup>a\*</sup>
<sup>a</sup>Department of Electrical and Computer Engineering, Iowa State University of Science and Technology, Ames, IA USA 50011

#### ABSTRACT

Understanding the dynamic behavior of photopolymers in nanoscale environment is essential to improving MEMS/NEMS device fabrication technologies. Here, we unveil the highly nonlinear behaviors of photopolymers exhibited during the process of light-controlled, low-pressure nanoimprinting. Such peculiarities can complicate the relation between the UV-dose and the height of the nanoimprinted feature, degrading the accuracy of the height control. To address the issue, we establish a theoretical process model and used the control of the nanoimprinting height for structural coloring applications. Our findings will broadly benefit nanotechnology and nanoscience.

# 1. INTRODUCTION

Recently, UV-curable photopolymers are gaining widespread adoption in nanoimprint lithography thanks to their ease of use in the fabrication process<sup>1,2</sup>. However, our understanding of the UV-curable photopolymer's fluidic behavior in the nanoscale structures is still very limited. This lack of understanding arises first from the absence of the effective means to observe the polymer's behavior in the nanoscale cavities with sufficient temporal and spatial resolutions. This study seeks to overcome this limitation by employing a photo-fluidic control to capture the progress of polymer's behavior, which leads to the modulation of the filling height. The results can be interpreted in the framework of a "low-pressure nanoimprinting" process which exploits the UV pre-curing of the photopolymer as the control mechanism<sup>2,3</sup>. This technique not only enables high-precision monitoring of the polymer's behavior but also introduces a novel approach to print nanoscale features with varying heights.

## 2. METHODS

The photopolymer of choice for this process is NOA 73 (Norland Inc). While our low-pressure nanoimprinting process shares similarities with the conventional UV nanoimprint process, a key departure is the pre-curing step that occurs before it contacts the PDMS template. Through the pre-curing, we could modulate the height of the resulting nanotexture<sup>2,3</sup>. Firstly, the master mold was created using two-photon polymerization lithography (TPL) through a Nanoscribe GmbH Photonic Professional GT2 system as depicted in Figure 1a. We designed a ridge array with fixed pitch  $\sim$ 3  $\mu$ m, width  $\sim$  1.5  $\mu$ m, and height 1.2  $\mu$ m (Sample A).

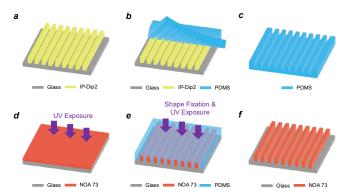


Figure 1. A schematic diagram of the fabrication process (a) The master mold fabrication through TPL, (b) PDMS replication, (c) Low-pressure nanoimprinting, (d) Pre-curing of NOA 73 with UV light, (e) Conformal contact and shape fixing by an additional UV exposure. (f) Release.

In this process, IP-Dip2, a UV-curable photopolymer, was applied to a fused silica substrate. The substrate was then transferred to the Nanoscribe system, where the structure was patterned using a laser power of 25 mW and a laser scan speed of 5000 µm/s. After the patterning process, the substrate underwent a 10-minute immersion in propylene glycol monomethyl ether acetate (PGMEA) solution to remove the uncured photopolymer. Subsequently, the substrate was immersed in isopropyl alcohol for 5 minutes to clean the residue and dried in ambient air conditions with UV curing under 15 mW/cm². Following the completion of the master mold fabrication, poly(dimethylsiloxane) (PDMS) replication was carried out. It was prepared with a 10 (base):1 (curing agent) weight ratio, poured onto the master mold, and cured for 10 hrs at 70 C. Finally, the cured PDMS was peeled off from the master mold.

#### 3. RESULTS

Figure 2a shows the final heights hf of the nanoridges from Sample A ( $h = 1.2 \mu m$ ) as a function of the UV exposure time. In principle, hf should be inversely proportional to the UV dose as the UV pre-curing reduces the polymer volume available for the imprinting<sup>2,3</sup>. While such an inverse proportionality is evident, the curve is highly nonlinear with a very noticeable gap in the middle. The existence of such a gap in the cavity filling process couldn't have been revealed without this UV-controlled nanoimprinting technique. A possible gap formation mechanism is summarized in Figure 2b.

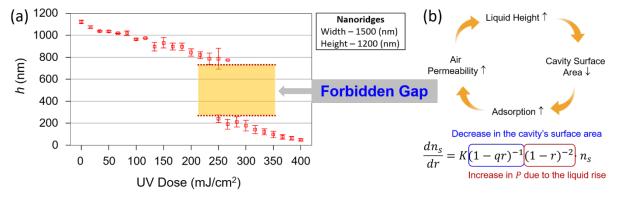


Figure 2. (a) The final heights  $h_f$  of the nanoridges from Sample A ( $h_o = 1.2 \mu m$ ) as a function of UV exposure time. The gap appeared at UV exposure time ~108 s, limiting the h range from 0.33  $\mu m$  to 0.88  $\mu m$ . (b) A schematic diagram summarizing the hypothesized gap formation mechanism. The evaporation of organic molecules from NOA 73 and the change in the cavity volume lead to a positive feedback loop which induces the sudden liquid height change.

## 4. CONCLUSIONS

A new nanoimprinting technique was developed to enable high-resolution spatial modulation of feature height. The process also allowed step-by-step monitoring of the nanoimprinting process and revealed the highly nonlinear dynamics of the process. The nonlinearity was attributed to a possible positive feedback among the liquid motion and molecule evaporation.

## **ACKNOWLEDGEMENTS**

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