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Citation: AIP Advances 7, 035110 (2017); doi: 10.1063/1.4978448 View online: http://dx.doi.org/10.1063/1.4978448 View Table of Contents: http://aip.scitation.org/toc/adv/7/3 Published by the American Institute of Physics

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## High-resolution nanopatterning of biodegradable polylactide by thermal nanoimprint lithography using gas permeable mold

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(Received 6 December 2016; accepted 28 February 2017; published online 8 March 2017)

We report high-resolution (150 nm) nanopatterning of biodegradable polylactide by thermal nanoimprint lithography using dichloromethane as a volatile solvent for improving the liquidity and a porous cyclodextrin-based gas-permeable mold. This study demonstrates the high-resolution patterning of polylactic acid and other non-liquid functional materials with poor fluidity by thermal nanoimprinting. Such a patterning is expected to expand the utility of thermal nanoimprint lithography and fabricate non-liquid functional materials suitable for eco-friendly and biomedical applications. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4978448]

Biodegradable polylactide is a thermoplastic aliphatic polyester derived by the polymerization of lactic acid, which is obtained from corn or potatoes, and is expected to be a viable alternative to petrochemical-based biomass polymers.<sup>1–5</sup> Polylactide has attracted much attention as a recycling biomass resource for the development of an environment-friendly society. Polylactide has excellent mechanical and optical properties, which make it suitable for use in the manufacture of various materials such as sheets, films, nonwovens, tapes, containers, fibers, and ropes.<sup>6–8</sup>

However, it is difficult to create high-resolution nanopatterned (up to a few hundred nanometers) polylactide surfaces using methods such as mold injection, which involve etching-less direct patterning, hot embossing, and nanoimprint lithography. This is because polylactide exhibits non-liquid properties at room temperature and poor fluidity at high temperatures.<sup>9–12</sup> In addition, it is a solid at room temperature and shows poor melt stability at temperatures higher than 130 °C because it undergoes hydrolysis and thermal degradation.<sup>13,14</sup> Low resolution sub-micropatterning of polylactide has been reported previously.<sup>15–18</sup> According to some reports, the fluidity of polylactide and non-liquid nanoimprint transfer materials with high viscosity is inevitably sacrificed for smooth filling of the mold during mold injection, hot embossing, and imprinting.<sup>19–22</sup> Polylactide with a high-resolution nanopatterned surface is required for functional and biomedical applications such as anti-adhesive films, water repellent tapes, optical grating sheets, anti-reflection materials, and anti-microbial films.<sup>23–31</sup>

In our previous studies, we reported several eco-friendly functional materials derived from biomass resources (especially porous cyclodextrin-based gas-permeable mold materials) for the expanded use of thermal and ultraviolet (UV) nanoimprint lithography and biomass resources.<sup>32–38</sup> Porous cyclodextrin-based gas-permeable mold materials were prepared in order to minimize solvent and gas trapping, which result in incomplete filling of the patterning materials in the mold during imprinting.<sup>39,40</sup> In nanoimprint lithography, a gas-permeable mold allows the use of volatile solvents with improved fluidity in nanoimprint transfer materials.<sup>41,42</sup>

The objective of this study was to expand the resolution limit of polylactide nanopatterns so that their biodegradability as well as mechanical and optical properties are enhanced for the aforementioned applications. High-resolution (150 nm) nanopatterns were created by thermal nanoimprint



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lithography using both a gas-permeable mold made of porous cyclodextrin with an average pore size of approximately 0.7 nm and a nanoimprint transfer material of polylactide containing dichloromethane as a volatile solvent. The results showed that the nanopatterns of polylactide, which is a solid at room temperature and has poor melt stability because of its susceptibility to hydrolysis and thermal degradation, were suitable for the applications mentioned above.

Double nanoimprint lithography methods using second-imprinting of polylactide with a volatile solvent (used for maintaining liquidity in the thermal nanoimprint lithography process) and a porous cyclodextrin-based gas-permeable mold were demonstrated. The second-imprinting was carried out after first-imprinting the porous cyclodextrin-based gas-permeable mold by using a quartz master mold during the UV nanoimprint lithography process. The quartz master mold featured approximately 150 nm line and 150 nm space dense patterns with a depth of 100 nm and an area of 5 mm<sup>2</sup>.

The quartz master mold was drawn using an electron beam lithography system (CABL-8000TPU, Crestec) and a water developable resist material developed by us at Toyama Prefectural University.<sup>43,44</sup> DS-831TH (DURASURF, Harves) was used as a fluorinated self-assembled monolayer. Prior to use, it was treated for 5 min using an ozone generator (LTOZ-180, Litho Tech Japan) to achieve a clear separation between the quartz master mold and the transferred porous cyclodextrin-based gas-permeable mold. DS-831TH was applied to the quartz master mold by immersing the slides for 1 min and then drying them for 1 min. The surface treated quartz master mold was then rinsed for 1 min with DS-TH (DURASURF, Harves) followed by drying for 1 min.

The porous cyclodextrin-based mold material was dispensed on a novolac-based adhesion underlayer-coated substrate.<sup>39,40</sup> The quartz master mold was then brought into contact with the porous cyclodextrin-based gas-permeable mold material for 10 min at room temperature so that the recesses of the approximately 150 nm line and 150 nm space dense patterns in the quartz master mold were filled by capillary force. Once the porous cyclodextrin-based mold material had completely filled the features on the quartz master mold, UV polymerization of the porous cyclodextrin-based mold material was carried out by using a metal halide lamp system (Sun Energy, broad band targeted for the 365 nm peak, irradiation intensity = 58 mW/cm<sup>2</sup>, irradiation time = 10 min). The porous cyclodextrin-based mold material was then maintained at 130 °C for 3 h under reduced pressure after the UV irradiation for drying.

Figure 1 shows the schematic of the second-imprinting of the synthesized polylactide solution containing dichloromethane as a volatile solvent for maintaining the liquidity during the thermal nanoimprint lithography by using the aforementioned pattern transferred porous cyclodextrinbased gas-permeable mold. The thermal nanoimprint material was prepared by adding 20 wt% dichloromethane into polylactide, which is a solid at room temperature and shows poor fluidity even after being heated, for increasing its fluidity. The nanoimprint transfer material containing polylactide and dichloromethane was dropped and pressed on the silicon wafers with a coated novolac-based adhesion underlayer material that we prepared in our previous studies.<sup>45,46</sup> This underlayer material was spun on the silicon wafers at 4000 rpm for 60 s and then cross-linked at 205 °C for 60 s.

The nanoimprint transfer material containing polylactide and dichloromethane was pressed at 350 N for 2 min at room temperature. It filled the features on the porous cyclodextrin-based gas-permeable mold. Heating was performed at 75 °C for 8 min by increasing the temperature gradually from room temperature. Dichloromethane was separated from the nanoimprint transfer material during this heating process. The porous cyclodextrin-based gas-permeable mold was then removed from the nanopatterned polylactide surface. The silicon wafers were subjected to thermal nanoimprint lithography cycles with a single porous cyclodextrin-based gas-permeable mold. The pattern profiles of polylactide were observed by scanning probe microscopy (SPM; SPM-9700, Shimadzu).

Figure 2 shows the SPM image of pattern failure by pattern projection round loss for a polylactide solution containing 20 wt% dichloromethane (volatile solvent) in thermal nanoimprint lithography using a referenced non-gas permeable quartz mold. Volatile solvents such as dichloromethane were used to increase the fluidity of polylactide for creating high-resolution nanopatterned surfaces (less than 500 nm) by using imprinting methods. However, the use of volatile solvents with low molecular

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FIG. 1. Schematic of imprinting of polylactide and dichloromethane solution by thermal nanoimprint lithography using porous cyclodextrin-based gas-permeable mold with 150 nm line and 150 nm space dense patterns. Dichloromethane was used as a volatile solvent for improving liquidity.

weight in nanoimprint transfer materials results in pattern failure because of solvent and gas trapping when a non-gas permeable mold made of a metal, silicon, or quartz is employed. The use of these volatile solvents or flow improvers caused pattern failure.

Figure 3 shows the chemical structures of (a) polylactide; (b) dichloromethane which was used as a volatile solvent to increase the fluidity of polylactide; (c) cyclodextrin derivatives with acryloyloxyalkyl groups in the porous cyclodextrin-based gas-permeable mold; (d) a UV initiator for the radical polymerization of acryloyloxyalkyl groups; (e) novolac resins with hydroxyl and epoxy groups in the underlayer previously reported by us; (f) 1,3,4,6-tetrakis(methoxymethyl)glycoluril, which was used as a cross-linker to react with hydroxyl groups; and (g) pyridinium p-toluenesulfonate, which was used as a thermal initiator.

Polylactide with an average molecular weight of 5000-10000 was synthesized by a two-step chemical reaction, which involved lactide formation and subsequent ring opening polymerization of the lactide to form a lactic acid cyclic dimmer. In the first part of the chemical reactions, the stannous octoate (Tokyo Chemical)-catalyzed polymerization of lactic acid (Tokyo Chemical) was carried out at 245 °C. The water generated by the union of the monomer was removed by a vacuum process. In the second part, the ring-opening polymerization of the lactide took place. Stannous octoate was used as a catalyst and 1-dodecanol (Tokyo Chemical) was used as a polymeric initiator. The lactide was heated at 130 °C after stirring at 150 °C and then purified after removing the unreacted lactide monomer.



FIG. 2. Image of 150 nm line pattern failure by pattern projection round loss of polylactide solution containing volatile solvent in thermal nanoimprint lithography carried out using non-gas permeable quartz mold.



FIG. 3. Chemical structures of (a) polylactide, (b) dichloromethane which was used as volatile solvent, (c) cyclodextrin derivatives with acryloyloxyalkyl groups, (d) UV initiator for radical polymerization of acryloyloxyalkyl groups, (e) novolac resins with hydroxyl and epoxy groups, (f) 1,3,4,6-tetrakis(methoxymethyl)glycoluril as cross-linker to react with hydroxyl groups, and (g) pyridinium p-toluenesulfonate as thermal initiator.

The resulting polylactide was subjected to gel permeation chromatography (GPC; HLC-8320GPC EcoSEC, Tosoh). The GPC system comprised two separation columns SuperAW3000 and SuperAW-H (TSK-GEL, Tosoh). *N*,*N*-dimethylformamide was used as the mobile phase and PStQuick Kit-H (Tosoh) was used as the polystyrene standard. The column temperature was maintained at 40 °C. The solvent flow rate was set at 0.6 mL/min.

The porous cyclodextrin-based gas-permeable mold material with an average molecular weight of 3000 was developed according to the procedure reported in our previous studies.<sup>39,40,46</sup> The porous cyclodextrin-based gas-permeable mold material was formed by the chemical reaction of 2-acryloyloxyethyl isocyanate (Showa Denko) with the hydroxyl group of 2-hydroxypropyl-beta-cyclodextrin (Cyclochem). 2-Hydroxypropyl-beta-cyclodextrin was blended with 2-acryloyloxyethyl isocyanate and methyl ethyl ketone. 5 wt% triethylamine (Tokyo Chemical) was added to the solution. The solution was then stirred at 60 °C under a nitrogen atmosphere during the water-inhibition chemical reaction. The porous cyclodextrin-based gas-permeable mold material was blended with dextrin oligomer and additives including 2-hydroxy-2-methyl-1-phenyl-1-propanone, which was used as a UV initiator for the radical polymerization.

The novolac-based adhesion underlayer material with an average molecular weight of 4000 was also prepared as reported in our previous studies,<sup>46</sup> via the chemical reaction of benzoic acid (Tokyo Chemical) with the epoxy group of epoxy novolac resins D.E.N. (Dow Chemical). The solution was then stirred at 98 °C in the presence of benzyltriethylammonium chloride (Tokyo Chemical) as a catalyst.

Figure 4 shows the (a) first, (b) second, and (c) fifth cycles of the 150 nm dense line nanopatterning of polylactide. The line widths of polylactide after the (a) first, (b) second, and (c) fifth nanoimprinting cycles were measured to be  $151 \pm 6$ ,  $153 \pm 7$ , and  $153 \pm 9$  nm, respectively. The line heights of polylactide after the (a) first, (b) second, and (c) fifth nanoimprinting cycle were measured to be 99  $\pm 2$ , 99  $\pm 2$ , and 98  $\pm 3$  nm, respectively. The 150 nm dense line patterns of polylactide with poor







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(c)
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Reduction of pattern failure

FIG. 4. 150 nm resolution patterning images of polylactide after (a) first, (b) second, and (c) fifth cycle.

fluidity were realized by thermal nanoimprint lithography by using the porous cyclodextrin-based gas-permeable mold and the nanoimprint transfer material made of polylactide, with dichloromethane as a volatile solvent. The dependence of thermal nanoimprint lithography cycles on the measured line widths and heights of polylactide was assumed to be within the variability of the line width roughness of SPM images. To obtain high-resolution patterning (<100 nm) and various patterns such as pillars or holes, the manual separation process must be replaced by a mass production process comprising step and repeat technologies, which involve field-by-field deposition and exposure of the nanoimprint transfer material with high fluidity by blending with a volatile solvent. In addition to the step and repeat technologies in nanoimprint processes, the release lifetime of the porous cyclodextrin-based gas-permeable mold was a key parameter of the properties. The development of new surfactants treated on the gas-permeable mold is expected for easy demolding.

With the nanopatterning method proposed in this study, it is possible to avoid pattern failure due to solvent trapping when a non-gas permeable quartz mold is used, as shown in Fig. 2. The oxygen transmission rates of the porous cyclodextrin-based gas-permeable mold, non-gas permeable quartz mold, and referenced polyethylene (a gas permeable material) were measured using a gas barrier and transmission rate testing system GTR-11 (GTR Tec). This system used gas chromatography with a differential pressure method capable of measuring the oxygen transmission rate. 47,48 The thickness of each sample was approximately  $100 \,\mu\text{m}$ , and the temperature was  $40 \,^{\circ}\text{C}$ . The oxygen transmission rates of the porous cyclodextrin-based gas-permeable mold, non-gas permeable quartz mold, and referenced polyethylene were approximately  $310 \times 10^{-12}$ , less than  $0.1 \times 10^{-12}$ , and  $270 \times 10^{-12}$  cm<sup>3</sup>·cm/cm<sup>2</sup>·s·cm Hg, respectively. From the characterization results for the porous cyclodextrin-based gas-permeable mold, it can be concluded that the high-resolution patterning of polylactide with dichloromethane was related to the gas permeability of the mold and fluidity of the material used for filling the mold smoothly during the pressing time before heating. Oxygen transmission rate is an indicator of the gas and solvent permeability of the mold. A specific analysis method for measuring the transmission rate of the actual volatile solvent in the mold will also be investigated.

In summary, the high-resolution (150 nm) nanopatterning of biodegradable polylactide using a porous cyclodextrin-based gas-permeable mold and a nanoimprint transfer material consisting of polylactide along with dichloromethane as a volatile solvent was successfully carried out by thermal nanoimprint lithography. The proposed method reduced the probability of pattern failure. This study portends a breakthrough in the use of not only polylactide but also other non-liquid functional materials with poor fluidity for eco-friendly and biomedical applications and for the expanded use of thermal nanoimprint lithography.

#### ACKNOWLEDGMENTS

This work was supported by JSPS Grant-in-Aid for scientific Research No. 16K04920, JSPS Bilateral Joint Research Projects, and Regional Innovation Strategy Support Program, Toyama Nanotech Cluster 2014 of Ministry of Education, Culture, Sports, Science and Technology, Japan. This project was also partially supported by The Die and Mould Technology Promotion Foundation, The Amada Foundation, The Naito Taisyun Science and Technology Foundation, and The Takeuchi MFG Foundation. The author is deeply grateful to Professor C. Grant Willson of the University of Texas at Austin for his encouragement.

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