Effective fabrication of three-dimensional nano/microstructures in a single step using multilayered stamp

Sang-Hu Park, Tae-Woo Lim, and Dong-Yol Yang[a)]
Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

Jun-Ho Jeong and Ki-Don Kim
Nano-Mechanical Systems Research Center, Korea Institute of Machinery and Materials, Daejeon 305-343, Korea

Kwang-Sup Lee
Department of Polymer Science and Engineering, Hannam University, Daejeon 306-791, Korea

Hong-Jin Kong
Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

(Received 10 February 2006; accepted 18 April 2006; published online 15 May 2006)

A technique in ultraviolet nanoimprint lithography (UV-NIL) for the creation of three-dimensional (3D) nanopatterns in a single step is proposed. The single-step fabrication of 3D or multilevel structures has a multitude of benefits. Inherent in this is the elimination of a need for alignment for multilevel fabrications as well as being a cost effective and simple process. For 3D UV-NIL, a trial in the fabrication of multilayered stamps has been conducted employing two-photon polymerization and diamondlike carbon (DLC) coating technique. The DLC coating layer enables the polymer patterns to be used effectively as a stamp without the need for an antiadhesion material. Additionally, O_2-plasma ashing has the potential for an epoch-making improvement of the precision of polymer patterns with a linewidth of 60 nm. Overall, several fine patterns are imprinted using the multilayered stamp onto a UV-curable resist via a single-step process without any identifiable damage. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2204448]

Nanoimprint lithography (NIL) is known as an emerging lithography with a resolution of less than 10 nm, having a high throughput and low cost compared to the conventional photolithography.[1–5] In ultraviolet (UV) NIL, a nanopatterned UV-transparent stamp is pressed onto a spin-coated resin on a substrate and then cured by UV light.[3] This process demands only a low pressing pressure and can be done at room temperature, which has some advantages compared to the thermal-type NIL. Until now, most of the research works concerned with NIL are focused on two-dimensional (2D) patterning for mass production. However, the fabrication of three-dimensional (3D) nano/microstructures is of great importance in diverse fields of modern technology for the development of highly functional applications. From this point of view, some 3D nano/microfabrication techniques have been developed using nonphotolithographic approaches. Among them, two-photon polymerization (TPP) is considered as a promising technique and has been extensively studied over the last decade in order to fabricate complex 3D micro/nanodevices by a method of stacking layers.[6–14] TPP is considered currently as a unique technique that could create a real 3D microstructure with a high spatial resolution beneath the limit of diffraction of light. More detailed explanations on TPP are given in numerous reports.[8–14] However, a high processing time is normally required to create 3D microstructures due to the intrinsic TPP characteristic of the layer-by-layer accumulation. For this reason, TPP is evaluated as an incongruent process for mass production in spite of its unique capability of complete 3D micro- and nanoscale fabrications. Therefore, in being the latest, the increase of throughput in TPP becomes an important issue for its practical use as a nanofabrication process.[15–17]

In this work, the fabrication process of a 3D multilayered stamp besides, applicable to UV-NIL and has a resolution of sub-100-nm scale, is introduced for the fabrication of 3D or multilevel nano/microstructures in a single-step. The single-step fabrication of multilevel structures has some meaningful advantages of avoiding an alignment issue of several 2D stamps (or masks) including the low fabrication cost due to a single stamp and a simple process. Figure 1 summarizes the fabrication procedure of the 3D multilayered stamp for UV-NIL, which consists of four different parts: a glass plate, polymer patterns, a diamondlike carbon (DLC) layer, and a thick glass plate for reinforcement. On a thin glass plate, 3D polymer patterns were created using TPP. For this work, an optical femtosecond laser system has been utilized. The full specifications on the developed system were given in our previous reports.[8–10,12] Through these procedures, 3D polymer patterns on the thin glass plate were created for use as an UV-NIL stamp with the advantages of a flexible design, as well as being perfectly transparent to UV light.

Another important issue concerned with TPP that comes into being in recent research works is how to improve the resolution of microstructures. In general, it is well known that the resolution in TPP is dependent on the process parameters such as laser power and exposing time. The previous works have shown that the high spatial resolution of a voxel could be achieved with a delicate control of the laser dose

[a)]Author to whom correspondence should be addressed; elecronic mail: dyyang@kaist.ac.kr

 © 2006 American Institute of Physics
Downloaded 14 Apr 2011 to 143.248.233.201. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

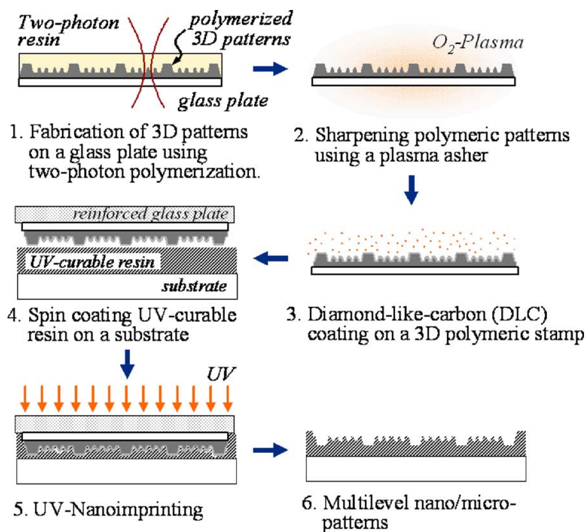

FIG. 1. (Color online) Schematic illustration of the fabrication procedure of the multilayered stamp and the UV-nanoimprint process for the creation of nano/micropatterns in a single step.

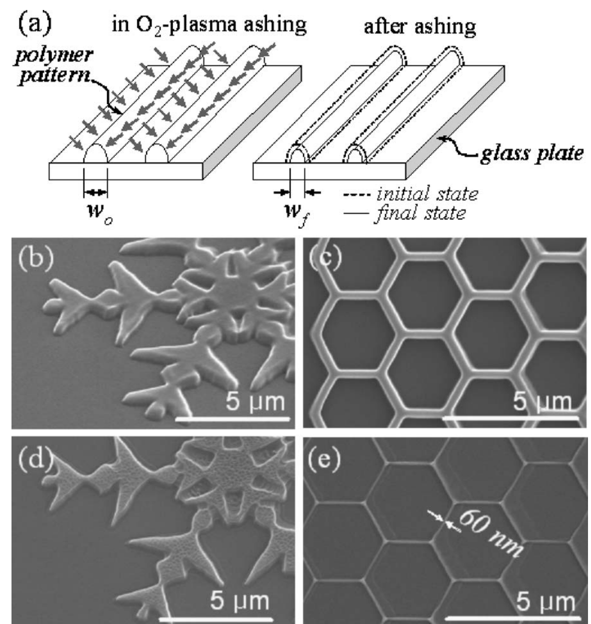

FIG. 2. (a) Schematic illustration of O_2-plasma ashing effect. The initial linewidth (w_o) is reduced to the thinned linewidth (w_f) by the ashing process. Scanning electron microscopy (SEM) images of 2D polymer patterns before and after O_2-plasma ashing; [(b) and (c)] the initial state of patterns fabricated by two-photon polymerization. Images of (d) and (e) are the thinned patterns by the O_2-plasma ashing corresponding to (b) and (c), respectively. The linewidth in the honeycomb structure becomes 60 nm from the 280 nm of the initial image.

into the near-threshold energy region for polymerization.[7–10] Moreover, an approach using a radical quencher to improve the resolution of a voxel has been reported in a recent study,[18] in which a lateral spatial resolution of 100 nm was achieved using the quenching effect. However, in case the quenching effect is utilized, the mechanical strength of the polymerized structure is inevitably reduced, despite achieving a high spatial resolution, because of the smaller molecular weight of polymerized structures.[19] Therefore, a challenging issue related with the enhancement of the mechanical strength still remains when it comes to the practical use of radical quenchers in the 3D nanofabrication.

An approach using an O_2-plasma cleaner (this is originally utilized for surface treatment and clean) as a secondary process for improving the resolution of microstructures created by TPP has been attempted in this work. As shown in Figs. 2(b)–2(e), the polymerized patterns created by TPP can be sharpened in the atmosphere of O_2 plasma. An initial line pattern with a linewidth of 280 nm has turned into a sub-100-nm (approximately 60 nm) in linewidth after plasma ashing under the conditions of plasma powers of 50 W_f and 11 W_r, a working pressure of 400 mTorr, and an ashing time (t) of 6 min. The ashing rate (η) is about 36.6 nm/min defined as $\eta=(w_o-w_f)/t$, where w_o and w_f indicate the original and thinned linewidths after the plasma ashing, respectively [Fig. 2(a)]. The sub-100-nm linewidth, by this time, is not easily created by the TPP process alone. Separately comparing Figs. 2(b) and 2(c) (*before ashing process*) with the corresponding images in Figs. 2(d) and 2(e) (*after ashing process*), it can be noted that the pattern shapes become dramatically thin and sharp edged. This ashing process is also applicable to the 3D microstructures by the same thinning mechanism. These results show that the O_2-plasma ashing process can be effectively utilized as a secondary process of TPP for improving a resolution and sharpening 2D and 3D polymer microstructures, although the surface state of the sharpened structures becomes fairly rough, caused by the attack of O_2 plasma after the process. However, these defects are expected to be minimized by an optimal control of the ashing conditions.

A stamp for UV-NIL is normally coated with an antiadhesion layer such as an alkysiloxane self-assembled monolayer (SAM) to reduce the incidence of patterning failure due to adhesion between the stamp and the resist layer. However, the reiterative imprinting causes the durability of the SAM to diminish depending on the process parameters: imprint pressure, resin properties, and aspect ratio of patterns.[3] Therefore, the periodic redeposition of an antiadhesion layer onto the stamp is required. Incidentally, the DLC is well known to have the advantages of lower surface energy, lower friction, and higher hardness. The contact angle between UV-curable resins and a DLC layer was measured to be about 70°. These excellent properties are of importance in many applications in diverse areas.[20] Thus, when DLC is coated onto polymer patterns, the periodical redeposition of antiadhesion layer is not needed; in addition, the mechanical strength of the polymer patterns is to some extent increased due to the high strength of DLC. In order to evaluate the increase of hardness by DLC coating quantitatively, nanoindentation tests were conducted. Two polymer squares sized in 1.5 mm in thickness and 3.0 mm in width were prepared to compare the hardness between one with the DLC coating of 20 nm in thickness and the other sample (original polymer square). In the test results, it is shown by observing the shallow indentation depth (~20 nm) that a considerable, fivefold (approximately) increase in hardness was obtained in case the DLC coating was present.

Despite this, a thick DLC layer has a shortcoming of low UV transparency, therefore the control of the DLC coating thickness is of importance to ensure UV transparency for use as a UV stamp. In the preliminary tests on the UV transparency depending on a DLC coating thickness, a polymer layer coated with the DLC of 100 nm allows passing UV light of 10%–13%. In case of a coating thickness in excess of

Downloaded 14 Apr 2011 to 143.248.233.201. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

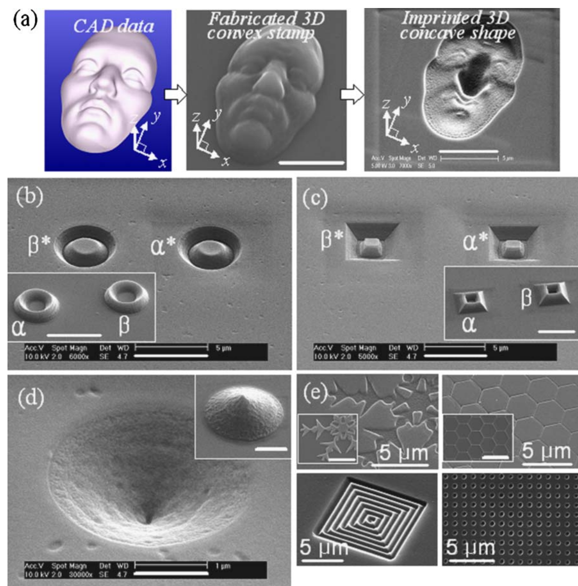

FIG. 3. (Color online) SEM images of some imprinted 3D and multilevel structures; (a) schematic sequential procedures of creating 3D face shape from designed shape to imprinted result: computer-aided design (CAD), SEM image of fabricated 3D convex face shape (*stamp*, the scale bar is 5 μm), and 3D concave shape (*imprinted result*). [(b) and (c)] Imprinted two circular rings and two rectangular rings (α^*, β^*); the inserts are the image of corresponding multilayered stamps (α,β), and all scale bar is 5 μm. (d) Imprinted cone-shaped microstructure (shown in the insert, the scale bar represents 1 μm). (e) Various imprinted 2D patterns; the inserts are the image of fabricated stamps.

500 nm, the UV transparency is found to be close to 0%, similar to an opaque material. However, the DLC coating of less than 10 nm is found to have a UV transparency of approximately 80% with a good anti-adhesion characteristic. For this reason, the multilayered stamps were fabricated, in this work, with a DLC coating of around 10 nm on the superficial polymer patterns. However, more efforts are needed to evaluate explicitly the variation of antiadhesive qualities depending on various thicknesses of DLC coating between the stamp and the resist.

Figures 3(a)–3(e) show some fabricated 3D concavoconvex multilayered stamps as well as their corresponding UV-imprinted results. The used photoresist in UV-NIL was a homemade UV-curable resin whose major component is tripropylene glycol diacylate (TPGDA) with the imprint conditions of an exposure intensity of 14.4 mW/ cm^2, an exposure time of 60 s, and an imprint pressure of 930 mbars. Under these imprinting conditions, the stamp is undamaged, because the mechanical properties of Young's modulus, of 3.5 GPa and a yield stress, of 20–40 MPa are realistic values for many glassy polymers and photoresists.[21] From the results, excellent correlations between 3D mutilayered stamps and imprinted features can be observed without any problem. These results indicate that multilevel nano- and microscaled structures can be created in a single step using the multilayered stamps.

In summary, the applicability of 3D multilayered stamps to a 3D UV-NIL process was demonstrated for the fabrication of 3D or multilevel patterns in a single step. This process has the benefits of cost-effectiveness and mass-production capabilities, as well as being a simpler process. Additionally, it negates the alignment issue of a multilevel process. Furthermore, the plasma ashing process is utilized as a secondary process for the resolution enhancement of 3D patterns, and the amount of ashing is readily controlled by the exposure time. Through the sharpening process, a pattern of nearly 60 nm in linewidth is achieved from the original linewidth of 280 nm. The thin layer characteristic of DLC has some excellent features applicable to 3D UV-NIL. However, intensive investigations into the lifetime usefulness, the yields of the antiadhesion, and the variation of the coating thicknesses of a DLC layer still remain to be resolved by further studies. Overall in this work, several 3D nano/micro patterns were created in a single step by the 3D UV-NIL process, and these results demonstrate the possibility of the application of TPP as the multilayered stamp.

The authors give thanks to Korean Ministry of Science and Technology (project of research for development of fundamental nanotechnology, M10503000217-05M0300-21700) for financial supports. One of the authors (J.H.J. gives thanks to the Center for Nanoscale Mechatronics & Manufacturing, one of the 21st Century Frontier Research Programs for financial supports (Project No. M102KN01001).

[1]S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Science **272**, 85 (1996).
[2]S. Y. Chou, C. Keimel, and J. Gu, Nature (London) **417**, 835 (2002).
[3]J. H. Jeong, Y. S. Sim, H. K. Sohn, and E. S. Lee, Microelectron. Eng. **75**, 165 (2004).
[4]M. D. Austin, H. Ge, W. Wu, M. Li, Z. Yu, D. Wasserman, S. A. Lyon, and S. Y. Chou, Appl. Phys. Lett. **84**, 5299 (2004).
[5]Q. Xia, C. Keimel, H. Ge, Z. Yu, W. Wu, and S. Y. Chou, Appl. Phys. Lett. **83**, 4417 (2003).
[6]H.-B. Sun, V. Mizeikis, Y. Xu, S. Juodkazis, J.-Y. Ye, S. Matsuo, and H. Misawa, Appl. Phys. Lett. **79**, 3173 (2001).
[7]H.-B. Sun, K. Tanaka, M.-S. Kim, K.-S. Lee, and S. Kawata, Appl. Phys. Lett. **83**, 1104 (2003).
[8]S. H. Park, T. W. Lim, D.-Y. Yang, H. J. Kong, K. S. Kim, and K.-S. Lee, Bull. Korean Chem. Soc. **25**, 1119 (2004).
[9]S. H. Park, T. W. Lim, S. H. Lee, D.-Y. Yang, H. J. Kong, and K.-S. Lee, Polymer (Korea) **29**, 146 (2005).
[10]S. H. Park, S. H. Lee, D.-Y. Yang, H. J. Kong, and K.-S. Lee, Appl. Phys. Lett. **87**, 154108 (2005).
[11]J. Serbin, A. Egbert, A. Ostendorf, B. N. Chichkov, R. Houbertz, G. Domann, J. Schulz, C. Cronauer, L. Frohlich, and M. Popall, Opt. Lett. **28**, 301 (2003).
[12]T. W. Lim, S. H. Park, and D. Y. Yang, Microelectron. Eng. **77**, 382 (2005).
[13]S. Kawata, H.-B. Sun, T. Tanaka, and T. Kenji, Nature (London) **412**, 697 (2001).
[14]C. A. Coenjarts and C. K. Ober, Chem. Mater. **16**, 5556 (2004).
[15]S. Matsuo, S. Juodkazis, and H. Misawa, Appl. Phys. A: Mater. Sci. Process. **80**, 683 (2005).
[16]J. Kato, N. Takeyasu, Y. Adachi, H.-B. Sun, and S. Kawata, Appl. Phys. Lett. **86**, 044102 (2005).
[17]C. N. LaFaratta, T. Baldacchini, R. A. Farrer, J. T. Fourkas, M. C. Teich, B. E. A. Saleh, and M. J. Naughton, J. Phys. Chem. B **108**, 11256 (2004).
[18]K. Takada, H.-B. Sun, and S. Kawata, Appl. Phys. Lett. **86**, 1071122 (2005).
[19]D.I. Bower, *An Introduction to Polymer Physics* (Cambridge University Press, Cambridge, 2002).
[20]X.-M. He, M. Hakovirta, and M. Nastasi, J. Phys.: Condens. Matter **16**, 8713 (2004).
[21]K. Yoshimoto, M. P. Stoykovich, H. B. Cao, J. J. de Pablo, P. F. Nealey, and W. J. Drugan, J. Appl. Phys. **96**, 1857 (2004).

Downloaded 14 Apr 2011 to 143.248.233.201. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions