

# Large Area Replication of AAO Nanostructure Using A Solvent Exchange Method and UV-Curable Polymers

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## ABSTRACT

An effective insertion in spontaneous mechanism of fluidic polymer precursors into nanometer-scaled holes is realized for the exact replication of nanopatterns in large area. The noble ideas for the spontaneous insertions are based on the explicit principles of physical chemistry; bringing the negative pressure in the holes by ammonia gas to fill the water out and the stepwise exchanges of the fluidic filled materials in spontaneous way. A series of pore type films of anodized aluminum oxide (PTF AAO) is fabricated by the well-defined hole-patterns as the template molds. The spontaneous insertions of fluidic precursors are successfully demonstrated into the nano-holes for polymer patterning in  $5 \times 5 \text{ cm}^2$  area using 4-hydroxybutylacrylate, ethyleneglycol-diacrylate, pyrrole, and the commercially available precursor 311RM.

**Keywords:** nanopattern, replication, anodized aluminum oxide

## 1 INTRODUCTION

Polymer-based nanopatterns have taken critical roles on the recent expansions of science and commercial technologies on various areas [1-3]. Polymers offer an easy fabrication for nanopatterns. The physical properties of them are also tunable for desired utilizations in technical level. The direct replication by nanoimprinting method [4-8] is known to be one of the effective ways for polymer patterning. It is fast, and applicable for preparing a specific complex structure. Industrially, the high throughput producing with low cost is also able to be realized through this technique. But it is not suitable for large area fabrications because of the bubble trapping troubles and of the requirement for high processing temperature near of glass transition temperature for the employed polymer.

The cross-linking of polymeric precursors in a template mold is an excellent alternative method for a large area patterning [9, 10] avoids those troubles, but there has been another occurring obstacle for a precise patterning. In many cases for the template-based replication techniques [11-17], anti-sticking agents have usually been applied on the surface of the employed template mold for easy departure of the patterned substrate from it. However it is surely

helpful for a convenient departure, it essentially reduces the critical surface tension of the applied mold surface. Then, if the mother template mold has deep and narrow pores with low critical surface tension than the surface tension of the engaged fluidic precursor, there is no guarantee for the perfect insertion of the fluidic precursor into the every pores to the bottoms.

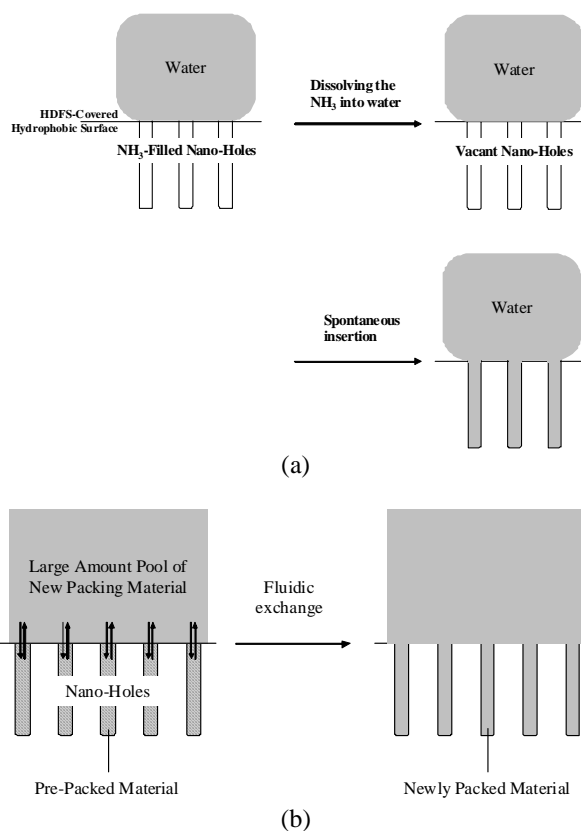


Figure 1: Schematic views for the spontaneous insertion mechanism: There is no spontaneous way for insertion of water if environmental air is filled in the nano-holes, but (a) the  $\text{NH}_3$ -filled nano-holes make possible for the spontaneous insertion. Then, (b) the newly packed material is filled up by a spontaneous exchange from the relatively large amount pool.

Therefore a systematic method is required for filling the pores up with fluidic polymeric precursors. That is why there have been many reports indicate that a specific pressure should be applied on the cohered substrates through the fluidic precursor for an effective insertion. Here, we report a systematic and guaranteed method for inserting the fluidic precursors into every nano-holes of porous mother template over the large area at least  $5 \times 5 \text{ cm}^2$  even if the surface of the template has been chemically modified by an anti-sticking agent of low critical surface tension. Through the withdrawal effect of ammonia-filled holes and a sort of stepwise exchanges of fluidics, several kinds polymeric precursors are successfully inserted into the nano-holes of the well-controlled molds of anodized aluminum oxide (AAO) which has been chemically modified with heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (HDFS).

AAO is one of the suitable templates for realizing the idea of the exact negative replication of polymeric pattern, because the hole-pattern of AAO has excellently defined orders: The pore type film (PTF) of AAO has gain big interests in the wide range of science and technology for nanofabrication, since the noble method for obtaining a highly ordered pattern of hexagonally packed pores was reported by Masuda and coworkers [14-15]. Technologically, the most significant advantage of the well ordered PTF AAO is that the sizes and the feature of the pattern are easily controllable in nanometer scale by the simple controls of experimental factors; choice of an acidic electrolyte for its self-ordering regime, and the exposing time to the electrochemical field for its growth to determine the height of the pattern.

## 2 EXPERIMENTS

A series of PTF AAO molds for the replication had been prepared under the precisely controlled conditions of anodization. The O-70, P-200, and P-370 AAO molds were fabricated on 99.999% aluminum plates (purchased from Goodfellow, Penn.) successfully in the acidic anodization solutions; oxalic acid for O-70 and phosphoric acid for both P-200 and P-370. Thus, the self-ordering regimes of the AAO molds are 110 nm for O-70 and 500 nm for both P-200 and P-370, respectively. These are well matched with the reported values. The hole-depths have been controlled by the lengths of various anodization times as 1 min, 30 min, and 50 min for O-70 (120 nm), P-200 (350 nm) and P-370 (600 nm) respectively. Finally, the widths of the holes have been controlled as 70 nm for O-70, 200 nm for P-200 and 370 nm for P-370, respectively by the additional post-etching processes in 5% phosphoric acid without the applied voltage.

The fabricated AAOs have been rinsed with ethanol and dried in vacuum desiccator thoroughly for more than 3 hours. Then, the surfaces of every AAO molds are modified with self-assembled HDFS monolayer as an anti-sticking layer for easy departure: The dried AAOs had been dipped

into a 3 mM HDFS solution of n-hexane for 10 minutes, and the thorough rinsing of the surface with HFE-7100 (3M, Mn.) was followed. Finally, the HDFS-covered AAOs have been dried in vacuum desiccator for an hour.

The well-modified HDFS-covered AAO substrate has a hydrophobic surface. The obtained static contact angles to a water-droplet and 311RM (Minutatech, Korea) precursor are  $136^\circ$  and  $70^\circ$ , respectively. In order to achieve a perfect insertion of the polymeric precursors to the bottoms of the nano-holes in the hydrophobic surface, we have taken a sort of systematic procedure as follows: The PTF AAO molds were placed in a cattle reactor filled with  $\text{NH}_3$  gas for 20 min. The mold has been moved into deionized water (DIW) quickly, and to be kept in for 10 min.

The AAO of water-filled nano-holes has been moved to the second pool of ethanol with an enough volume (200 mL in this study) to be kept in for 10 min. Then finally, the ethanol-soluble polymeric precursor 311RM was applied without reinforced pressure on the mother molds but for the spontaneous exchanges of the precursor into the holes from the relatively large amount pool. The schematic view for the spontaneous filling of water and the stepwise exchange are shown in Figure 1.

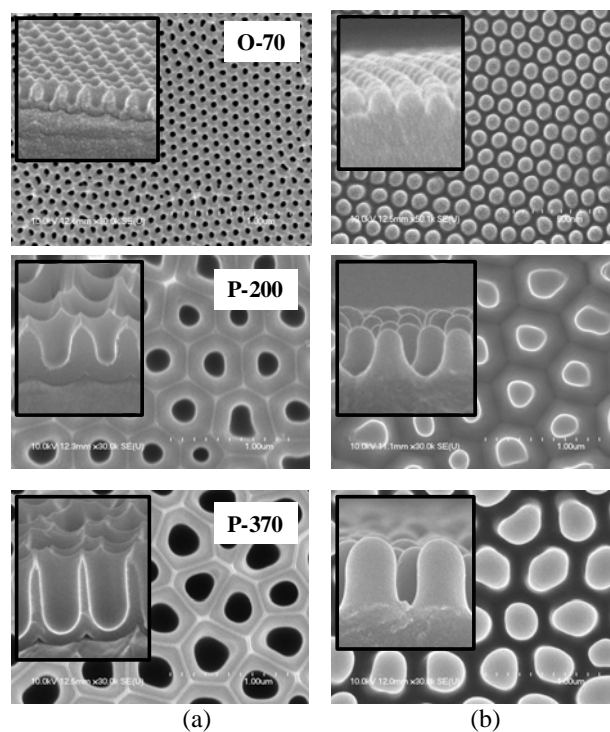


Figure 2: SEM images of (a) the mother AAO templates, O-70, P-200 and P-370, and (b) the exactly replicated negative patterns on 311RM. The cross-sectional images are in the boxes.

## 3 RESULTS AND DISCUSSIONS

Because of the incredible solubility of ammonia for water (52.0 g / 100ml at 20 °C, about 700 times of volume for the gas phase ammonia is soluble into water), it is expected that the most of ammonia in the every holes is dissolved immediately into the relatively large amount pool of DIW: The total volume of the holes at the surface of 5 x 5 cm<sup>2</sup> sized O-70 AAO is estimated only as 0.23 μL. It is relatively very small volume even if the plate is dipped into a 100 mL of DIW. That kind of sudden dissolving causes a shattering vacancy in the holes as a local vacuum to withdraw water effectively from the large pool even if the AAO surface is modified as a hydrophobic or a superhydrophobic surface.

As shown in Figure 2, the negative patterns of the PTF AAOs have been successfully transferred to the polymerized substrates of 311RM with the nanometer-scale precision by this approach. Especially, the depths of the mother AAO molds are exactly replicated to the polymeric patterns; 100 nm for O-70, 320 nm for P-200, and 570 nm for P-370, respectively. These are very acceptable values by the considerations of the thickness of bottom layers; 20 nm for O-70, and 30 nm for P-200 and P-370, respectively.

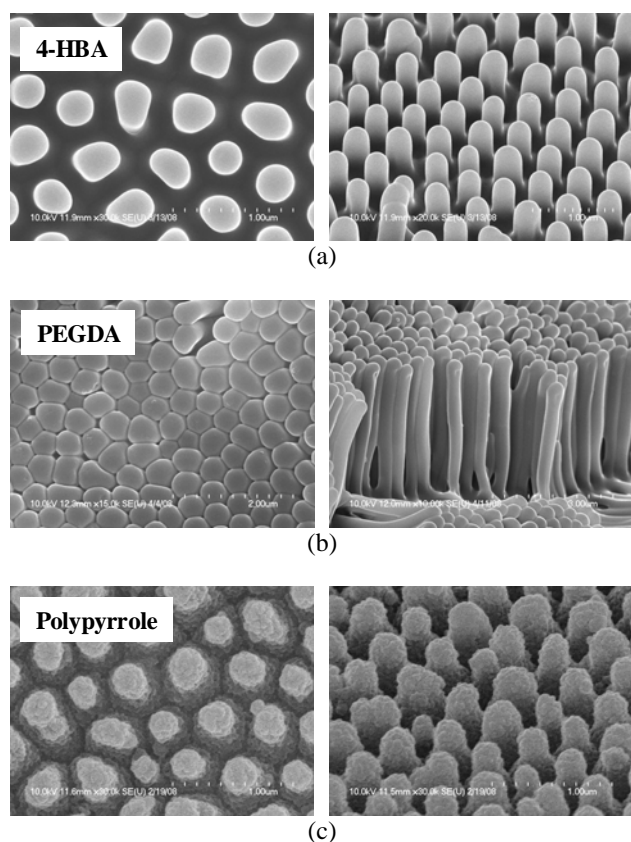


Figure 3: SEM images of (a) 4-HBA, (b) PEGDA and (c) polypyrrole patterns, replicated from the PTF AAO in our systematic approach.

There are several remarkable points on this approach. Firstly, this approach is applicable to other polymeric precursors. Figure 3 shows the other examples of pillar pattern replications using 4-hydroxybutylacrylate (4-HBA), poly(ethyleneglycol)diacrylate (PEGDA), and pyrrole under the same procedure for 311RM. Second, the applicable depth of this approach on nano-holes is expanded to micrometer-scaled pattern with the high aspect ratio (Figure 3 (b)). Thus, it can be an important technical basis for the easy preparing a nano-pattern of functional polymer, such as the electro-conductive polypyrrole (Figure 3 (c)) as the desired features in nanometer-scale. Finally, the patterning area of the polymer substrate can be expanded to cm scale. Figure 4 shows the picture of the original AAO template (left-side) and the negatively replicated pattern (right-side) of 311RM. We successfully have achieved the precise replication on the 5 x 5 cm<sup>2</sup> area in this study, and it is expected that more large area of the patterning is possible.

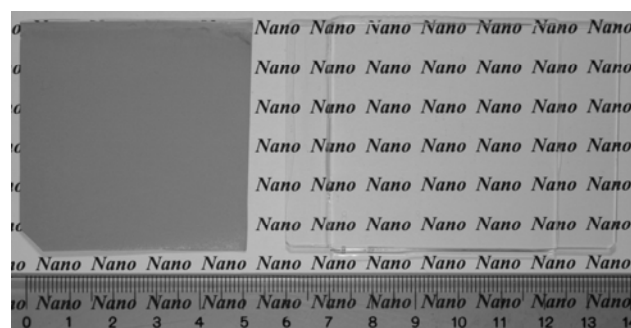


Figure 4: The original AAO pattern (O-70, left-side) and the replicated negative pattern (311RM, right-side).

## 4 ACKNOWLEDGEMENT

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## REFERENCES

- [1] P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W. Gymer, "Chemical tuning of electroluminescent copolymers to improve emission efficiencies and allow patterning" *Nature*, 356, 47-49, 1992.
- [2] R. Langer and J. P. Vacanti, "Tissue engineering", *Science*, 260, 920-926, 1993.
- [3] N.A. Peppas A. Khademhosseini, R. Langer, "Hydrogels in Biology and Medicine: From Molecular Principles to Bionanotechnology", *Advanced Materials*, 18, 1345-1360, 2006.

- [4] S. Y. Chou, P. R. Krauss and P. J. Renstrom, "Imprint of sub-25 nm vias and trenches in polymers", *Applied Physics Letters*, 67, 3114-3116, 1995.
- [5] S. Y. Chou, P. R. Krauss and P. J. Renstrom, "Imprint Lithography with 25-Nanometer Resolution", *Science*, 272, 85-87, 1996.
- [6] S. Y. Chou, P. R. Krauss and P. J. Renstrom, "Nanoimprint lithography. In: The 40th international conference on electron, ion, and photon beam technology and nanofabrication", (Atlanta, Georgia (USA): AVS), pp 4129-4133, 1996.
- [7] H. Tan, A. Gilbertson and S. Y. Chou, "Roller nanoimprint lithography. In: Papers from the 42nd international conference on electron, ion, and photon beam technology and nanofabrication", (Chicago, Illinois (USA): AVS) pp 3926-3928, 1998.
- [8] D.-Y. Khang, H. Kang, T.-I. Kim and H. H. Lee, "Low-Pressure Nanoimprint Lithography", *Nano Letters*, 4, 633-637, 2004.
- [9] S. Wang, G. J. Yu, J. L. Gong, Q. T. Li, H. J. Xu, D. Z. Zhu and Z. Y. Zhu, "Large-area fabrication of periodic Fe nanorings with controllable aspect ratios in porous alumina templates", *Nanotechnology*, 17, 1594-1598, 2006.
- [10] S. Wang, G. J. Yu, J. L. Gong, D. Z. Zhu and H. H. Xia, "Large-area uniform nanodot arrays embedded in porous anodic alumina", *Nanotechnology*, 18, 015303, 2007.
- [11] J. Liang, H. Luo, R. Beresford and J. Xu, "A growth pathway for highly ordered quantum dot arrays", *Applied Physics Letters*, 85, 5974-5976, 2004.
- [12] M. A. Ghanem, P. N. Bartlett, P. de Groot and A. Zhukov, "A double templated electrodeposition method for the fabrication of arrays of metal nanodots", *Electrochemistry Communications*, 6, 447-453, 2004.
- [13] Y. Lei and W.-K. Chim, "Shape and Size Control of Regularly Arrayed Nanodots Fabricated Using Ultrathin Alumina Masks", *Chemistry of Materials*, 17, 580-585, 2005.
- [14] H. Masuda, "Fabrication of Ordered Arrays of Multiple Nanodots Using Anodic Porous Alumina as an Evaporation Mask", *Advanced Materials*, 12, 1031-1033, 2000.
- [15] H. Masuda, "Fabrication of Gold Nanodot Array Using Anodic Porous Alumina as an Evaporation Mask", *Japanese Journal of Applied Physics*, 35, 1996.
- [16] W. J. Dauksher, N. V. Le, E. S. Ainley, K. J. Nordquist, K. A. Gehoski, S. R. Young, J. H. Baker, D. Convey and P. S. Mangat, "Nano-imprint lithography: Templates, imprinting and wafer pattern transfer", *Microelectronic Engineering*, 83, 929-932, 2006.
- [17] S. Grimm, R. Giesa, K. Sklarek, A. Langner, U. Goesele, H.-W. Schmidt and M. Steinhart, "Nondestructive Replication of Self-Ordered Nanoporous Alumina Membranes via Cross-Linked Polyacrylate Nanofiber Arrays", *Nano Letters*, 8, 1954-1959, 2008.