Regular Nano-Pores Fabricated By UV Cross-Linking Non-softbaked SU-8 Resist In a Solvent Evaporation Controlled Environment

[1]Chia-Jung Chang, [1*]Fan-Gang Tseng and [1,2]Chung-Shi Yang
[1]Engineering and System Science Department, National Tsing Hua University, Taiwan, ROC
[2]Department of Applied Chemistry, National Chi Nan University, Taiwan, ROC
* Engineering and System Science Department, National Tsing Hua University, Taiwan.
Tel: 886-3-5715131-4270, Fax: 886-3-5720724, E-mail: fangang@ess.nthu.edu.tw

ABSTRACT

This paper proposes a novel technology to fabricate 3D nano pore structures in SU-8 resist, a widely employed resist in MEMS and Bio-chips. Controlling the evaporation rate in SU-8 fabrication process, regular porous structures with pore size close to tens nm can be obtained. Fluorescent dye and glucose has been tested passing through this porous material while not through standard processed SU-8 resist film. This simple process provides a novel way to fabricate patternable molecular filter with SU-8 resist of regular nano sized pores.

Keywords: nano-pores , SU-8 resist, molecular filter, porous material

INTRODUCTION

SU-8 resist is a widely used photoresist in MEMS and also a biocompatible material [1]. However after cross-linking, it is an epoxy based material with very tight molecular structures lacking of nano-sized pores. Porous materials with nano sized pores can be fabricated one way by adding different kinds of monomers all together in a mixture to polymerize one to several types of monomers and then remove the rest of the materials to form porous structures [2, 3]. The other way is by controlling the solvent/solutes mixing ratio, then evaporating away the solvent and leaving behind the solutes to form porous structures [4]. However, in the first method, the polymer clusters may be trapped inside material posing structure not fully porous; on the other hand in the second method, not uniform and micro-sized structures are frequently formed in the process in stead of nano structures due to non-uniform cross-link/aggregation of solutes during the solvent evaporation. This study proposes a novel way by UV cross-link non-soft-baked SU-8 resist with abundant solvent to generate nano-sized 3-D spaces for controllable nano-pores formation.

EXPERIMENTAL

Fabrication

The fabrication concept of the molecular filter membrane is shown in Fig.1. Omni Coat was fist spun and baked on Silicon wafer as a release layer (Fig. 1a). SU-8 was left not soft-baked during UV-light exposure in a controlled environment for solvent to maintain saturated condition for defining nano hollow spaces in SU-8 resist (Fig. 1b). Pore size can be controlled by different solvent/SU-8 ratio. During the post exposure baking (PEB) process, solvent was driven out thoroughly from the already cross-linked nano pores structures in SU-8, as a result the pore size would not change much and remain its nano structures. The area of exposure can be utilized to define micro structures of the material. The porous SU-8 film was then released from silicon wafer after development process (Fig. 1c).

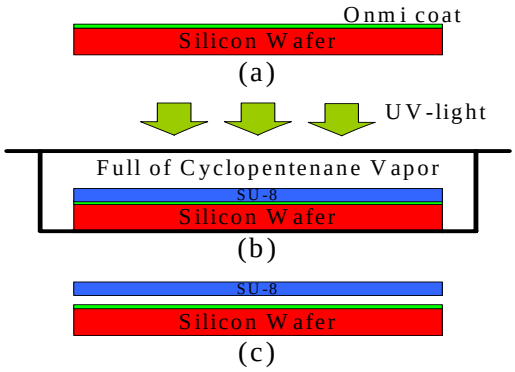

Fig. 1. Fabrication process of Porous SU-8

Controlling the solvent/SU-8 resin mixing ratio will produce a different cross-linking degree of the material. The SU-8 cross-linking concept is schematically shown in Fig. 2. In standard SU-8 resist process, most of the solvent is driven out during the soft baking process, leaving a very dense structure for exposure. As a result, the cross-linked SU-8 structures will be very tight to each other and lake of nano size gaps. On the other hand, the novel way proposed in this study performs UV exposure while SU-8 resist is still in liquid, or partial liquid condition, thus maintains many nano-sized pores among cross-lined SU-8 clusters. Since the cross linking process happens in a environment that solvent/monomer ratio is in a constant value, the already cross-linked nanoscale SU-8 clusters would not aggregate like in the solvent drying method [4] in which micro-sized structures will start to form during solvent-driven-out process.

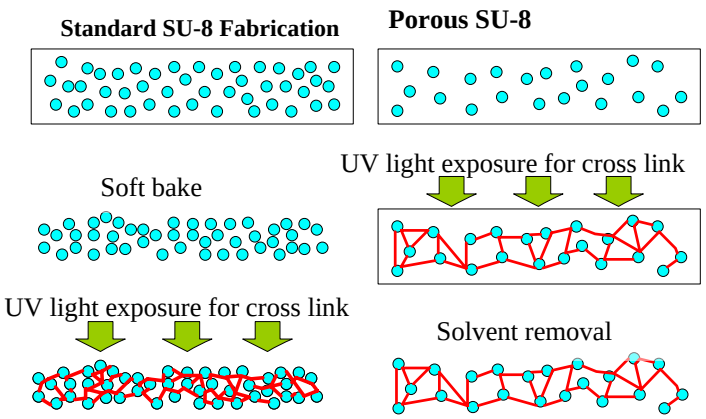

Fig. 2. The schematic of standard and porous SU-8 cross-linking process in SU8 developer, Cyclopentenane.

Testing

The fabricated porous SU-8 materials were tested by three methods to verify the fabricated nano pores have function for molecule penetration.

In the first test, fluorescence dye solution was directly dropped on the top of standard and porous SU-8 membranes of 35 μm thick for certain time to quickly see if fluorescence molecules can penetrate the membranes.

In The second test, the SU-8 films of 300 um thick were fixed in a Franz Cell as shown in Fig. 3. Glucose (50mM) was then adding on the top of the cell to test the molecule penetration ability of the films.

In the third test, in order to calculate the diffusion coefficient of molecules inside this material, SU-8 plates fabricated by different solvent/resin ratios were left inside Rhodamine 6G/DI-water solution for 80 hours at room temperature, as shown in Fig. 4. Samples were then broken into two pieces and checked under fluorescent optical microscope for fluorescence intensity measurement. The cross-section morphology of different materials were imaged by both field-emission-gun scanning electron microscope (FEGSEM, JEOL 6330F, Japan) and atomic force microscope (AFM, JPK, Germany) in contact mode. A commercial image process software, Image PRO plus (MediaCybernetics, USA), was employed to analyze the fluorescence intensity versus distance from the ourter boundary of the materials.

RESULTS

Fig. 5 and 7 show SEM images of standard SU-8 and porous SU-8, while Fig. 6 and Fig. 8 illustrate corresponding AFM images, respectively. The cross section of standard SU-8 reveals smooth surfaces and dense/continuous structures in Fig. 5 and 6... However, the ross section of porous SU-8 material appears rough and squama structures with a size close to 10-20 nm, as shown in Fig. 7 and 8.

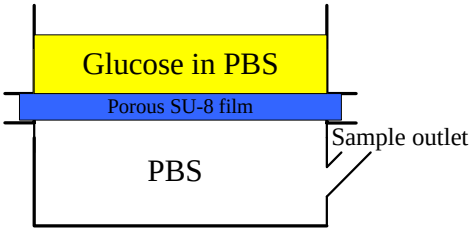

Fig. 3. Setup of Franz Cell for the testing of glucose cross-over rate in membrane.

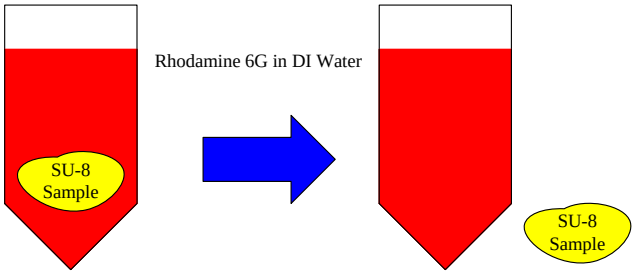

Fig. 4. Schematic of SU-8 plates immersion in in Rhodamine 6G solution for fluorescence diffusion testing.

In fluorescence dye testing, it is proved that Rhodamine 6G/Ethonal can pass through the porous film of 35 μm thick in one minute, leaving a stained area on the bottom of filter paper, but not through the standard SU-8 film (Fig. 9). It is also demonstrated that glucose can pass through the porous SU-8 film of 300 μm thick in 7 hours and the time sequence of concentration variation in the bottom Franz cell is shown in Fig. 10, demonstrating the capability of the porous SU-8 for the penetration of glucose molecules.

The cross section images of bulk porous SU-8 materials with 45% and 55% resin are shown in Fig. 11 and 13, respectively, having been in contact with Rhodamine 6G fluorescence for 80 hours. Their analyzed fluorescence intensities are calculated by Image PRO plus and shown in Fig. 12 and 14, respectively, demonstrating a molecule diffusion capability for the porous materials. Similar experiment has also applied to standard SU-8 bulk material, however, the penetration distance is at least two order of magnitude smaller than that of the porous ones even with 50% longer immersion time, as shown in Fig. 15 and 16.

Fig. 15 and Fig.16 are the fluorescence image of Rhodamine 6G which is diffused into standard soft-baked SU-8 in 120 hours at room temperature. There were nearly no diffusion occurs in standard fabrication process SU-8.

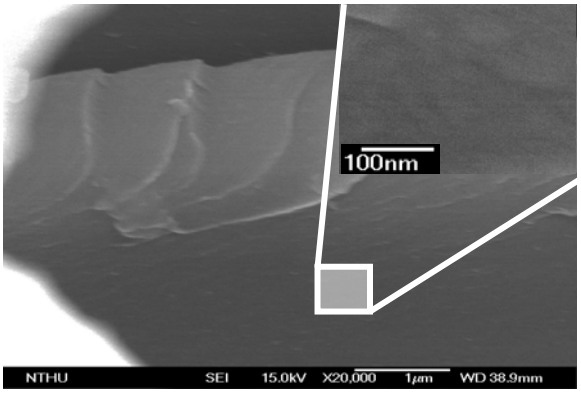

Fig. 5. The FEGSEM picture of the cross section of standard SU-8 2100 after fully cross link.

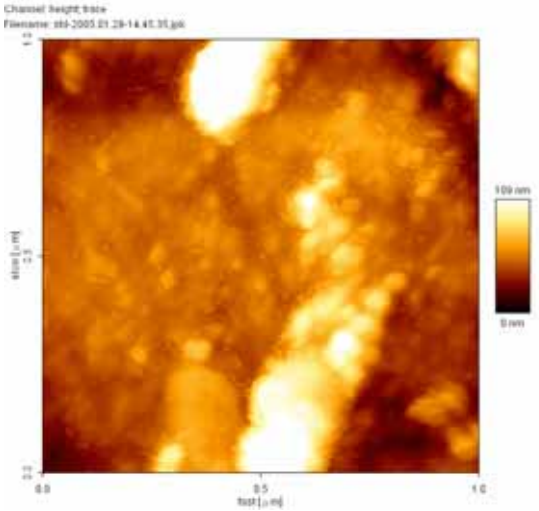

Fig. 6 The Tapping Mode AFM image of the cross section of standard SU-8 2100 after fully cross link.. Scanning area is 1umx1um.

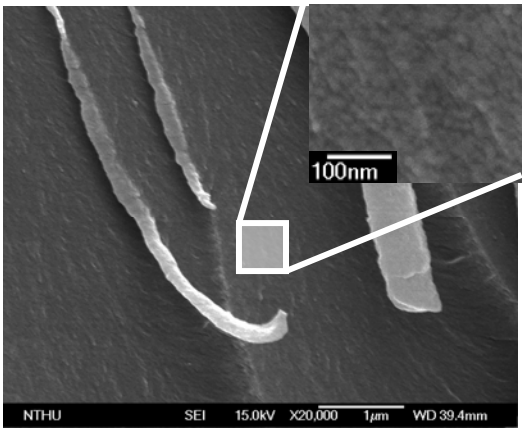

Fig. 7. The FEGSEM picture of the cross section of porous SU-8 materil after cross link.

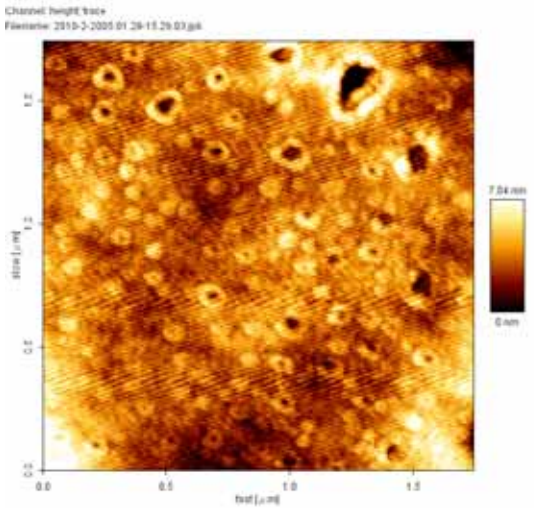

Fig. 8 The Tapping Mode AFM image of the cross section of porous SU-8 2010. Scanning area was 1.7umx1.7um.

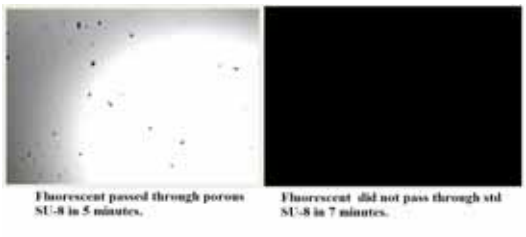

Fig. 9. Fluorescent testing of the cross over of Rhodamine 6G/Ethonal in SU-8 2035 (left) and standard SU-8 (right) films.

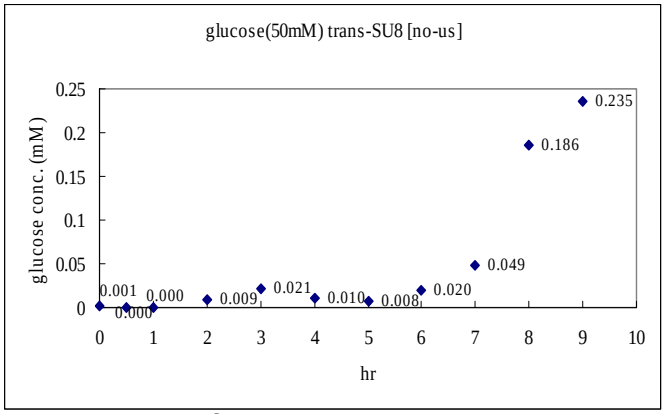

Fig. 10. 50mM Glucose cross-over testing on porous SU-8 films.

Fig.11 The fluorescence image of the cross-section for 45% Resi ı SU-8 in Rhodamine 6G solution for 80 hours. The scale bar is 250um.

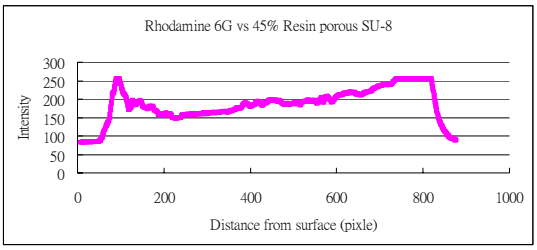

Fig. 12 The intensity profile of Rhodamine 6G diffused into 45% Resin SU-8 after 80 hours.

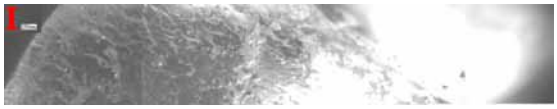

Fig. 13 The fluorescence image of the cross-section for 55% Resin SU-8 in Rhodamine 6G solution for 95 hours at room temperature. Scale Bar is 250 um.

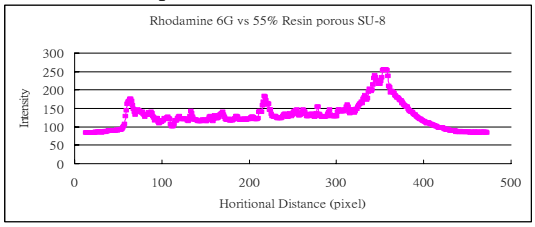

Fig. 14 The intensity profile of Rhodamine 6G diffused into 55% Resin SU-8 after 95 hours.

Fig. 15 The fluorescence image of the cross section of standard SU-8 in Rhodamine 6G for 120 hours. Scale Bar is 250um.

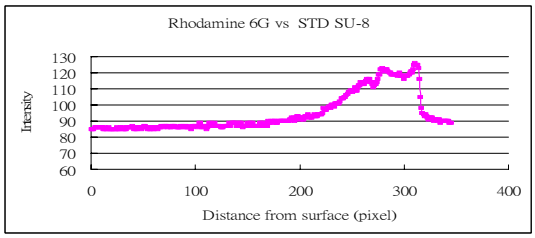

Fig. 16 The intensity profile of Rhodamine 6G diffused into STD SU-8 after 120 hours at room temperature.

DISCUSSION

From SEM images and AFM images, the squama structures in porous SU-8 might be the reason for glucose and Rhodamine 6G to pass through. After solvent evaporated from the cross-lined nano SU-8 cluster, nano-gaps are formed between the nano-cluster throughout the whole SU-8 material, not only on the surface. Those nano-gaps are closed to 10-20 nm according to the SEM images. In the diffusion distance testing experiment by Rhodamine 6G fluorescence, the lower SU-8 resin/ solvent ratio shows a longer fluorescence diffusion distance. The diffusion coefficient can be estimated by the following equation:

$$D = \frac{L_d^{\,2}}{2t} \qquad (1)$$

Where D is the diffusion coefficient and L_d is the diffusion length and t is diffusion time. The diffusion coefficients are calculated to be $2.312\text{x}10^{-11}$ m^2/sec for the 45% Resin SU-8 and $1.2005\text{x}10^{-11}$ m^2/sec for the 55% one, and both are calculated from the data at right side of the materials in Fig. 12 and 14. However, the diffusion distances in the same sample on the different sides are different. The estimated diffusion coefficient for the left side material of the 45% Resin SU-8 is $1.17045\text{x}10^{-12}$ m^2/sec (Fig. 12), around one order of magnitude lower than that of the right side material. This may result from the fabrication process in which the right side material was contacted with supporting substrate, while left side material was left upward. As a result, the left side material had much higher evaporation rate than that of the right side material, posing the formation of denser materials with smaller pores; while the right side material in contact with substrate had lower solvent evaporation rate, maintaining larger nano pores. However, in standard SU-8 material, there is almost no fluorescence molecules diffusion into the material, the near surface fluorescence intensity is very close to the background, as shown in Fig. 15 and 16.

CONCLUSION

By controlling the evaporation in SU-8 fabrication process, regular porous structures with pore size close to 10 nm can be obtained by direct UV exposure and monomer cross link. Fluorescent dye and glucose has been demonstrated passing through this porous material while not through standard processed SU-8 resist film. The diffusion coefficient for Rhodamine 6G into the 45% resin SU-8 material is higher than that in the 55% resin SU-8. This simple process provides a novel way to fabricate patternable micro structures with SU-8 resist of regular nano pores.

REFERENCES

[1] G. Voskerician, M. S. Shieve, R. S. Shawgo, H. von Recum, J. M. Anderson, M. J. Cima and R. Langer, Biomaterials 2003, 24, 1959-1967

[2] T. B. Stachowiak, T. Rohr, E. F. Hilder, D. S. Peterson, M. Yi, F. Svec, Jean M J. Frechet, Electrophoresis 2003, 24, 3689-3693

[3] C. Yu, M. Xu, F. Svec, J. M J. Frechet, Journal of Polymer Science Part A: Polymer Chemistry, 2002, Vol.40 755-769

[4] Q. Xie, J. Zu, L. Feng, L. Jiang, W. Tang, Xiangdong Luo, and C. C. Han, Advanced Materials, 2004, 16, No. 4, 302-305